



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>



Edw T 27 & 92, 115



HARVARD UNIVERSITY

LIBRARY OF THE

Department of Education

COLLECTION OF TEXT-BOOKS

Contributed by the Publishers

HARVARD COLLEGE  
LIBRARY



3 2044 097 019 053

440

A TEXT-BOOK  
OF  
INORGANIC CHEMISTRY

DESCRIPTIVE, THEORETICAL, AND PRACTICAL  
A MANUAL FOR ADVANCED STUDENTS

PART I  
*NON-METALLIC ELEMENTS*

BY

ALFRED A. BENNETT

PROFESSOR OF CHEMISTRY IN THE IOWA COLLEGE OF SCIENCE,  
AGRICULTURE, AND THE MECHANIC ARTS



SILVER, BURDETT & COMPANY

NEW YORK

BOSTON

CHICAGO

1892

✓ Educ T 228.92.215

**Harvard College Library**

**Dec. 20, 1918.**

**Transferred from  
Education Library.**

**COPYRIGHT, 1892,**

**By SILVER, BURDETT & CO.**

**TYPOGRAPHY BY J. S. CUSHING & Co., BOSTON.**

**PRESSWORK BY BERWICK & SMITH, BOSTON.**

## P R E F A C E.

---

THE aim of the writer in preparing this work has been to present the subject of chemistry from the experimental or laboratory side. It is the result of several years' experience in teaching the subject from this standpoint to large classes of students.

How to present the subject to students in order to reach the ends sought in education is a matter of great importance if chemistry is to form one of the subjects used in the general education of the youth. It certainly is not conducive to mind development to commit to memory the facts of chemistry, nor is it so to any high degree to pour the facts into the mind of the student, however entertainingly it may be done. It is the duty of the instructor to lead the student to think and to reason about facts and to draw conclusions from experimental data. Whenever it is possible, the student must discover the chemical facts about which he is to think and reason, if he is to receive the greatest mental benefit from the study. He should receive the intellectual benefit that comes from the discovery of truth; that is, of truth that is new to his mind. The fact itself is not as important to him as the study of its development, the conditions under which it is produced, and its relation to other facts.

In the experimental studies outlined in this book, the aim has been to tell the student as little as is possible, to lead him by question and suggestion to the facts to be established. These studies must precede the recitation on the general text,



and a discussion and explanation of these experiments should form a large part of the class-room work.

Long and minute descriptions of manipulation of apparatus are not generally given, since in most cases an exhibition of the method, or a blackboard sketch by the instructor, is far more satisfactory. The teacher, for example, can show in a moment how to collect gases over water, when a word description would occupy considerable space, and then will often not be understood.

Before the student begins the study of chemistry he must be familiar with the physical aspect of the subjects of heat and energy, and with the general properties of gases. The portion of the introduction referring to energy is merely a suggested review of this subject.

The order in which the study of the elements is taken up is not in accord with the recent tendency to consider them as they are arranged by the periodic law. The writer considers that the order adopted brings them before the student in the best manner for the development of the great body of the science of chemistry.

The periodic law is one of the latest generalizations from chemical facts and cannot be appreciated by the learner until he has viewed the whole field. The discussion of this law is consequently left for a later consideration. The study of potassium and sodium is introduced in order that the learner may have some facts to use in the consideration of acids and bases.

Again, the theoretical aspect of the subject is developed as the facts upon which these ideas rest are developed. The writer considers that it is productive of better results for the learner to study the facts upon which the laws of the science depend, and then to trace out the proper relations and draw the correct conclusions from them, than it is to learn these laws and theories apart from the other study. Formulæ are developed as the work progresses.

The student's note-book is the most important and valuable evidence of his advancement and understanding of an experimental science. A suggestion of an outline which he may use in writing up his experiments is given in the introduction. Every instructor is likely to have a method which he wishes to have followed ; but the note-book must be constantly at hand and must be constantly used if the student is to reach the best results.

The term "mass" is used throughout the text in place of "weight," since it expresses exactly what is meant, which is not true of the latter term.

Part II. of this work will be devoted to a consideration of the metals and the principles of qualitative analysis.

That student has received the most benefit from the study of chemistry who has been the most successfully led to think of things and their relations to each other, of the forces that may act upon them, and, in a word, to comprehend the true relations between causes and their effects. In the hope that this work will forward the laboratory method of teaching from the outset of the student's course, it is submitted to teachers of chemistry.

ALFRED A. BENNETT.

AMES, August, 1892.



# CONTENTS.

	PAGE
INTRODUCTION . . . . .	9
HYDROGEN . . . . .	25
CHLORINE . . . . .	32
BROMINE . . . . .	36
IODINE . . . . .	39
FLUORINE . . . . .	42
HYDROGEN AND CHLORINE . . . . .	44
HYDROGEN AND BROMINE . . . . .	48
HYDROGEN AND IODINE . . . . .	49
HYDROGEN AND FLUORINE . . . . .	50
OXYGEN . . . . .	68
WATER . . . . .	74
WATER — QUANTITATIVE COMPOSITION . . . . .	80
OZONE . . . . .	87
SODIUM . . . . .	91
POTASSIUM . . . . .	96
SULPHUR . . . . .	111
SULPHUR AND HYDROGEN . . . . .	116
SULPHUR AND CHLORINE FAMILY . . . . .	122
SELENIUM . . . . .	123
SELENIUM AND HYDROGEN . . . . .	124
TELLURIUM . . . . .	125
TELLURIUM AND HYDROGEN . . . . .	125
OXYGEN FAMILY . . . . .	126
NITROGEN . . . . .	129
NITROGEN AND HYDROGEN . . . . .	131
NITROGEN AND CHLORINE FAMILY . . . . .	142
AIR . . . . .	143
PHOSPHORUS . . . . .	146
PHOSPHORUS AND HYDROGEN . . . . .	153
PHOSPHORUS AND CHLORINE FAMILY . . . . .	158
ARSENIC . . . . .	159
ARSENIC AND HYDROGEN . . . . .	163

	PAGE
ARSENIC AND THE HALOGENS . . . . .	166
ANTIMONY . . . . .	167
ANTIMONY AND HYDROGEN . . . . .	170
ANTIMONY AND THE HALOGENS . . . . .	173
CARBON . . . . .	174
CARBON AND HYDROGEN . . . . .	184
SILICON . . . . .	192
SILICON AND HYDROGEN . . . . .	194
SILICON AND THE HALOGENS . . . . .	197
RECAPITULATION . . . . .	198
SULPHUR AND OXYGEN . . . . .	205
SULPHUR TRIOXIDE . . . . .	211
SULPHURIC ACID . . . . .	218
SELENIUM AND OXYGEN . . . . .	231
TELLURIUM AND OXYGEN . . . . .	231
NITROGEN AND OXYGEN . . . . .	232
NITROGEN OXIDES . . . . .	232
NITRIC ACID AND NITRATES . . . . .	244
OXIDATION AND REDUCTION . . . . .	258
PHOSPHORUS AND OXYGEN . . . . .	259
ARSENIC AND OXYGEN . . . . .	273
ARSENIC AND SULPHUR . . . . .	280
HALOGENS AND OXYGEN . . . . .	281
CARBON AND OXYGEN . . . . .	293
CARBON AND SULPHUR . . . . .	312
CARBON AND NITROGEN . . . . .	316
CYANOGEN . . . . .	318
COMBUSTION AND FLAMES . . . . .	318
SILICON AND OXYGEN . . . . .	329
BORON . . . . .	334
BORON AND HYDROGEN . . . . .	336
BORON AND THE HALOGENS . . . . .	336
BORON AND NITROGEN . . . . .	337
BORON AND OXYGEN . . . . .	338
GENERAL OBSERVATION AND RECAPITULATION . . . . .	341
CLASSIFICATION OF COMPOUNDS . . . . .	342
HYDRIDES . . . . .	343
HALIDES . . . . .	347
OXIDES AND HYDROXIDES . . . . .	347
FORMULÆ . . . . .	352

# INORGANIC CHEMISTRY.



## INTRODUCTION.

**Knowledge and Science.** — The human mind has accumulated knowledge in at least three directions: (*a*) knowledge of itself; (*b*) knowledge of time, space, and number; (*c*) knowledge of matter and energy. The facts in reference to time, space, and number, when co-ordinated and arranged, constitute the various branches of mathematics, *c.g.* geometry and algebra. The facts that have been ascertained as to the mind, and a statement of their relations to each other, constitute psychology, logic, and philology. The study of matter and energy (including the so-called vital energy) has developed the sciences of astronomy, physics, chemistry, botany, zoology, etc. A history of any one of these latter-named sciences might be considered an extended definition of a science. The earliest history of a science is the history of an accumulation of facts. This is followed in time by the discovery of certain relations existing between classes or groups of these facts; causes are assigned for the facts; new facts are discovered frequently as a result of these newly discovered relations. These relations are formulated into what are called laws. The discovery of facts and the establishment of laws go on as the science develops. A science is therefore a body of co-ordinated truths, and since there are truths yet undiscovered, science has not yet reached its complete development. This is especially true of the sciences relating to matter and energy,

**Matter and Energy.** — At the outset, the student should strive to get as clear a conception as is possible of what words stand for. What is matter? What is energy? are the first questions to be asked.

We see about us objects of various kinds, which we call bodies. We know certain facts in reference to these bodies. How have these facts been acquired? An examination shows that we have gained this knowledge through the use of the senses, *i.e.* through the use of the eye, the ear, the nose, the tongue, and the sense of touch. If any body, for example an apple, is examined, the eye discovers facts as to color, size, or extent; the nose, facts of odor; the tongue, facts of taste; and the touch, combined with the so-called muscular sense, tells us facts of mass. The two facts of extent in three directions and of mass are characteristic of all bodies or of all matter. Now that which constitutes or makes up bodies is called matter. Matter may therefore be defined as anything that occupies space, and is characterized by the properties of extension and mass.

A study of matter may lead to its classification into what we call kinds of matter, or to its arrangement in groups; *e.g.* sand, marble, plants, and animals. This classification is determined by external appearances. If the study is continued, it will be found that these portions of matter change in many ways. They may change position, color, structure, temperature, and, in fact, may undergo almost innumerable other changes. If a polished piece of iron is exposed to the air, its bright surface becomes covered with a reddish-colored matter; if a current of electricity is passed through it, it attracts other pieces of iron; if it is exposed to a high temperature, it becomes red. Energy in some of its many forms causes these changes. Energy is sometimes defined as the power to do work, as the power to overcome resistance; *i.e.* to change the position or relation of bodies or parts of bodies. Work is the act of producing a change in opposition to force.

**Forms of Energy.** — There are many forms of energy, such as heat, light, chemism, motion, and electricity. Each of these forms of energy may be accompanied by, and may be changed into, other forms. Examine, for example, the production of electrical energy, taking as the starting-point the burning of the fuel under the boiler. The chemical energy produced by the burning of the fuel is transformed into heat and light energy; by the water this energy is changed to molecular energy or energy of motion; this sets in motion the engine, which in turn starts the dynamo, which in its turn converts this motion into electrical energy. The electrical energy meets with resistance at the lamps and is converted into heat and light again.

**Phenomena.** — A more extended examination of nature will show that all matter is constantly undergoing changes which are almost infinite in variety and degree. Any one of these changes is called a phenomenon, or, in the form of a definition, a phenomenon is any change whatever in matter. It is an observed fact in reference to matter.

What matter is, without reference to the forces of nature, is not well understood. It is known that it has extent, or occupies space, and that it has mass; but of its structure, its ultimate constitution, but little is known. It is matter undergoing changes, or matter under the influence of energy, about which we have certain and definite knowledge.

**Experimental Study.** — Since the sciences, especially the physical sciences, are founded upon observed facts or phenomena, the question naturally arises, How shall they be studied? What is the object of this study? Shall the phenomena be observed, or shall we depend wholly on what somebody says who has observed them? Again, is it merely to observe phenomena, or do we seek something more? The mere fact of observation does not excite in the mind anything more than wonder, admiration, awe, and like feelings. The truly active



mind does not stop with mere observation, but attempts to comprehend and explain phenomena. Few people living in northern latitudes have not seen the Aurora Borealis. We are attracted by the beauty of Nature's display, and are led to express our admiration at the sublimity and grandeur of the scene. The mind, however, soon begins to question what the phenomenon is. But of all the questions asked is not the real one, What is the cause of this appearance? This idea of cause is founded on our belief that every effect has an adequate and unchanging cause, or, as expressed by the early writers, the cause must equal the effect. The cause of any phenomena can only be known to the observer when he knows all the conditions imposed upon the matter undergoing change. Generations of men have seen the Aurora Borealis without understanding it, because the conditions under which it was produced were not known. They could not reproduce the phenomena because they did not know the conditions under which they were produced. Now the production of a phenomenon, or of phenomena, is sometimes called an experiment, but there must be the added element of knowing under what conditions the phenomena are produced before it can be said to be a scientific experiment. Therefore an experiment may be defined as the production of a phenomenon, or of phenomena, under conditions known to the experimenter. In other words, it is more than mere observation which employs the senses alone; it demands the use of the highest mental faculties, such as reason, reflection, and judgment.

**Experimental Study, No. 1.** — (a) Examine a platinum wire (a piece of platinum wire about 5 cm. long and held in a handle made of glass tubing) to determine general appearances such as weight, hardness, flexibility, etc. Next place it for a minute or more in the flame of a Bunsen lamp. What changes occur? While hot test its flexibility. Remove it from the flame of the lamp and notice what changes occur. Weigh

it and compare it with what it was before it was placed in the lamp flame.

(*b*) Examine and study a piece of magnesium wire in exactly the same way. (When the wire is placed in the flame, be careful to save the products of the change.) Weigh the wire before and after the experiment. How does the product of the change compare with the original magnesium?

(*c*) Examine some fine iron filings (must be unoxidized) with a magnet. Examine sulphur in the same way. Next, mix thoroughly, in the mortar, 2 g. of iron filings and  $1\frac{1}{4}$  g. of powdered crystallized sulphur. Examine the mixture. Bring the magnet in contact with the mixture and withdraw it. Place a little of the mixture in a test-tube and add 5 cc. of bisulphide of carbon. Shake well and allow it to stand until the solution is clear. Turn off the clear solution and allow it to evaporate. What do these results show? Transfer another portion of the mixture to a dry test-tube and heat until the whole mass glows. Allow the tube to cool and then break it, examining the contents with a magnet. To a portion of the mass add a few drops of sulphuric acid. Note the odor of the escaping gas. Satisfy yourself that some change has occurred, and note what it is.

(*d*) Grind to a fine powder, in a mortar, sulphur and charcoal (carbon) in the proportions, by mass, of 16 to 3, respectively; compare them with the solution on your table labelled  $CS_2$ . This compound contains carbon and sulphur in the proportions just given; namely, 16 to 3. Note the differences.

What forms of energy have been used in *a*, *b*, *c*, and *d*? Examine these results in reference to changes produced in the matter acted upon.

**Physical and Chemical Phenomena.** — The results produced in experimental study No. 1 are typical of all ordinary changes produced in matter by the various forms of energy. In one set of changes there is no permanent alteration of the matter. In

another set of changes the matter is no longer the same matter, judged by its ordinary properties. The first class of changes is called physical changes or phenomena, and the second class constitutes chemical changes or phenomena. In general, it may be said that all changes in matter may be arranged in two great classes, on the basis of the effect produced on the matter being acted upon; namely, physical and chemical changes or phenomena. These two classes of phenomena are intimately related and might very properly be studied together. They are commonly studied under the two subjects of Physics and of Chemistry.

Chemistry, therefore, may be defined as the science which treats of the changes in matter by which its composition and its properties are altered. It should be noticed that the evidence of chemical changes is the fact that the new body possesses new physical properties as well as new chemical properties.

#### SOME OF THE CHARACTERISTICS OF CHEMICAL CHANGE.

**Experimental Study, No. 2.** — (a) Powder a few crystals of potassium chlorate and mix it with about an equal volume of sulphur. (Mix without grinding.) Has any change occurred? Heat a little of the mixture in 5 cc. of water in a test-tube. What has occurred? Put on a piece of writing-paper (about 5 cm.  $\times$  4 cm.) as much of the mixture as can be held on the point of a small knife-blade. Fold the paper tightly and place it on a solid body and strike it with a hammer. What was the cause of the report? Examine the contents of the paper. Is it then changed? What physical effect would the blow of the hammer have on the mixture? Examine each of the substances by itself in the same way.

(b) Place in a mortar a small bead of mercury and a few crystals of iodine. Gently rub them together with the pestle.

Is there a chemical change? What is the evidence of the change? What appeared to bring about this change? What physical effect was produced by the grinding?

(c) Mix equal volumes of *dry* bicarbonate of sodium and *dry* cream of tartar. Is there any evidence of chemical change? Next, take two small beakers, and place in one about 2 g. of sodium bicarbonate, and in the other 1 g. of cream of tartar. Add 15 cc. of water to each, stirring till both substances are dissolved. Now pour the solutions together. Is there chemical change? What is the evidence? What appeared to bring it about?

(d) Grind together, in a mortar, 1 g. each of sodium carbonate and litharge. Is there any evidence of chemical change? Make a conical depression in a piece of charcoal and place a portion of the mixture in it. Heat the mass on the charcoal to fusion with the blow-pipe flame, continuing the heat for a short time. When did the action begin? What was the cause of the change? What is one of the products?

(e) Take two test-tubes and place 5 cc. of hydrochloric acid in one, and 5 cc. of ammonia water in the other. Place them side by side and warm them in the lamp-flame. What is the evidence of chemical change? Carefully bring each tube near the nose. Is matter escaping? In what condition is it?

(f) Place in a dry test-tube 1 g. of cane sugar. Heat, noticing changes as they occur. Was there more than one kind of matter present? What is left in the tube? What was the cause of the change?

(g) Dissolve a crystal of silver nitrate in 10 cc. of water. (Do not touch the crystal or the solution with the fingers.) Prepare two strips of filtering-paper (10 cm.  $\times$  2 cm.). Dip each strip into the solution and immediately place one strip in a dark place, and the other in the sunlight. Examine each from time to time. Keep the strip in the dark for several

days. What is the evidence of chemical change here? What is the cause? Why?

(*h*) Dissolve 2 g. of lead acetate in 30 cc. of water in a beaker. Attach a rod of zinc, or strip of copper, 2 to 4 cm. long to the positive pole, and a strip of platinum to the negative pole, of a battery. Place them in the solution of lead acetate and allow them to remain there for several minutes. What is the deposit? What is the apparent cause of the change in this case?

**Conclusions from the Facts established.** — In (*a*) the sulphur and potassium chlorate were thoroughly mixed, but there was no evidence of chemical change. The sulphur was readily separated from the chlorate. When struck with the hammer, the two kinds of matter in the mixture were forced close together, and chemical action took place. Neither sulphur nor potassium chlorate when treated in the same way showed any evidence of chemical change.

In (*b*) there was chemical action produced by the slight pressure brought about by the rubbing or pressing of the two kinds of matter together.

In (*c*) no change was effected by the contact produced by rubbing or grinding the two bodies together. When the bodies were in solution, however, rapid effervescence did occur when the solutions were brought together, showing that chemical change was going on. Again, litharge, when mixed with sodium carbonate, gave no indication of change until heated to fusion on charcoal. Also, when the gas from ammonium hydroxide was brought in contact with the gas from hydrochloric acid, a new substance was formed.

It will be noticed that in (*a*), (*b*), (*c*), and (*d*) two kinds of matter have entered into the change. In (*e*) only one kind of matter was acted upon, and two or more kinds were produced; that is, chemical action may produce decomposition as well as combination. So far as these results may determine, it is

noticed, *first*, that the essential condition is that different kinds of matter must be brought so closely together that there is no sensible distance between the parts.

*Second.* That the kinds of matter must be dissimilar.

*Third.* That this condition of insensible distance may be brought about by mechanical means, — by solution, by fusion, and by vaporization.

*Fourth.* That the agents or forms of energy that are employed to aid or start chemical action, may be heat, light, and electricity. Also that this change may occur when no agent is used ; that is, that the change occurs by the mutual action of one substance on the other under the essential conditions. It is also true that while each agent may produce chemical action, the converse is true that chemical action may be produced by any one or all of these agents.

*Fifth.* Chemical change may be produced by heat when only one substance is acted upon.

**Forms of Matter.** — For the purpose of chemical study matter may be said to exist in three forms ; namely, as solids, liquids, and gases or aeriform bodies. In general, the solid body opposes resistance to change of shape and to change in size and has a self-subsistent form. The liquid body offers no resistance to change in shape, but does to change in size. The gaseous body offers resistance to reduction in size and tends to increase if not limited on all sides ; within proper limits, it may be said to increase indefinitely. The gaseous bodies are conveniently studied as true gases and vapors. The difference between them arises largely from the temperature to which they are exposed. At ordinary temperatures the vapors exist either as solids or as liquids.

All gases can be changed to the liquid or solid state if the temperature be reduced below a certain point, called the critical temperature, provided the pressure is sufficiently great.

The line of demarcation between these three states or forms

of matter is not clearly defined. In general, it may be said that the three forms of matter are due to the relative intensity of two opposing forces—one which tends to hold the parts or molecules of the body together, and another which tends to separate the parts or molecules of the body from each other. The first force is named cohesion, and the second is called heat. If the heat is great enough, all cohesion is overcome and the body becomes a gas.

Heat is the force which determines in which state the matter shall exist; *e.g.* iodine is a solid body at ordinary temperatures, but passes readily into the liquid and gaseous states under the influence of heat. Carbon, on the other hand, resists the action of heat and remains a solid at all temperatures. It is also true that vapors do not obey the law of Boyle at the temperature of formation, but at higher temperatures and at low pressures they do follow the law of volume and pressure. Gases, also, under high pressure and low temperature do not obey Boyle's law; that is, they act like vapors under these conditions.

**Physical and Chemical Properties.**—Any quality that belongs to matter is called a property of matter. In the study of any portion of matter three questions at least have always been asked; namely: How does it present itself to the senses,—that is, without reference to other kinds of matter? How does it act towards other matter? Does it contain more than one kind of matter, or what is its composition? The first question is answered by discovering the physical qualities of the substance, or, as it is commonly expressed, its physical properties. The second question is answered when the matter is brought in contact with other kinds of matter under conditions necessary to produce chemical change. When a portion of matter is thus completely examined, the experimenter is able to recognize and establish its individuality. These considerations lead to the definition of physical and chemical properties. Physical

properties are those qualities which distinguish a body as a mass. These properties are : (a) State of aggregation, — that is, is the body a solid, liquid, or gas ; (b) color, odor, taste ; (c) specific gravity and density ; (d) solubility, especially in water ; (e) (particularly for solids) lustre, hardness, malleability, ductility, brittleness ; (f) crystalline form.

The chemical properties of a body are those that distinguish it when brought in contact with other matter under conditions necessary to produce chemical change. By these two sets of properties all bodies are recognized and distinguished from one another.

The answer to the third question has been sought for from the earliest times. The Greeks endeavored to answer it by forming certain mental conceptions without reference to any examination of matter by experiment. Instead, therefore, of conceiving of matter as made up of indestructible units, with fixed and unvarying properties, they supposed matter to be of one kind, the apparent variety depending upon the presence of certain qualities, sometimes called elements. These elements were earth, water, air, and fire. The qualities represented by water were coldness and wetness ; those represented by earth were coldness and dryness ; those represented by the air were wetness and heat ; those represented by fire were dryness and heat. Water could be transformed into earth by heat. The usual natural waters hold in solution solid matter which is left when the water is converted into steam. This meant to them the conversion of water into solid matter, or earth. This illustrates only one of the many changes that matter might undergo according to these early writers.

**Elements and Compounds.** — Gradually the student of nature overthrew these conceptions and discovered that many kinds of matter could be separated by chemical means into other kinds, each kind possessing its own set of chemical and physical properties. Also, they discovered that two kinds of matter



could be made to assume, under the proper conditions, new properties, and thus become other kinds of matter. Again, they found that there were certain kinds of matter that could not be changed by any known process. Such substances are iron, silver, sulphur, etc. The iron and sulphur, when heated together in the right proportions, disappear as iron and as sulphur, yet they each may be found in the new substance, in kind and in quantity. Matter is, then, made up of units, which may exist free or may exist combined in such a way that the individual properties disappear and new substances are formed. The units are called elements, and the chemical combinations of units are called compounds.

It should be noted that what we now call an element may be a compound. It is possible that processes may be found by which the so-called elements may be separated into two or more kinds of matter. What we now know as potassium hydroxide was until about 1808 known as an element. Sir H. Davy then determined that it contained potassium, oxygen, and hydrogen.

To the chemist of to-day matter is composed of about seventy different elements, all other kinds of matter being a combination of two or more of these elements, each combination being called a compound. Only a few of these elements exist in large quantities.

**The Field of Chemistry.** — The study of chemistry, therefore, consists in an examination of these elements and their compounds for the purpose of learning their physical and chemical properties, and in the determination and study of the laws that govern their relations to one another.

**Symbols of Elements and their Compounds.** — The names of elements quite generally indicate some marked property possessed by them; e.g. the name of the element bromine is derived from a Greek word meaning a stench. It was so named because of the unpleasant odor of its vapor. Some-

times they indicate the country in which the element is principally or was at first found, as Germanium and Gallium. The termination "um" signifies a metal, and the termination "on" distinguishes the non-metals. The exceptions to this method of distinguishing the metals from the non-metals are in the names of those elements discovered during the early history of chemistry.

For convenience in representing the elements, their names are abbreviated to a single letter, or to two letters, the single letter always being the initial letter of the name of the element. If two elements have the same initial letter, usually the first and second letters are used, the second letter always being written as a small letter. In a few cases two elements have the same first two letters; then some other letter of the name is chosen; *e.g.* the symbol for boron is "B," for barium is "Ba," for Cæsium is "Cs," and not "Ca," since calcium was discovered first and "Ca" was appropriated for it.

Chemical compounds are represented by writing the symbols of the elements of which they are composed, one after the other, thus: KOH, HCl. These expressions are called formulæ (often symbols), and represent compounds consisting of the elements potassium (kalium), oxygen, and hydrogen in the first case, and hydrogen and chlorine in the second case.

**Conservation of Matter.** — The truth of the conservation of matter may be stated thus: Matter, as it is now known, cannot be destroyed or created by any method with which we now are acquainted. This fundamental truth, that on which chemistry rests, was not formulated until the last part of the eighteenth century. Chemists before this time generally believed that matter could be destroyed and created. They saw the plant start from the seed and develop into the full-grown tree without any apparent use of matter. They saw the same tree burned to ashes, whose bulk and weight were only a small fraction of that of the tree. Here was an apparent creation

and destruction of matter. It was only apparent. For matter in the soil and in the air contributed to increase the body of the tree ; in fact, not considering the matter contained in the seed, all the matter of the tree was supplied in this way. All of this matter returned to an invisible condition when the tree was burned, except the ash ; and although somewhat differently combined, if this invisible matter had been weighed as it escaped, and its weight added to that of the ash, it would be found to be equal to that of the original tree.

It is to Lavoisier that we owe the experimental demonstration of this great truth. This experiment has become a classic in the annals of chemistry. It would not be true to say that Lavoisier was the first to perform quantitative experiments in chemistry. The balance had been known in a fairly perfect condition for some time, and many quantitative results had been recorded. But to Lavoisier belongs the great credit of seeing beyond the results to the proper conclusion that followed from them. Since his time no experiments have in any sense contradicted this inference ; namely, that in all the changes going on in matter there is no increase or decrease in the total quantity of it in the universe.

**Conservation of Energy.**— This truth is commonly stated thus : If energy disappear in one form, it will reappear in one or more other forms. The quantity, however, will remain unchanged. Again, if  $a, b, c$ , etc., represent all the forms of energy, then  $a + b + c + d + \text{etc.} = A$ ,  $A$  being a constant quantity. Some of the recognized forms of energy are heat, light, electricity, cohesion, and chemism. If this law is applied to chemical energy, it says that no chemical energy is lost when chemical changes are produced in matter, but that it may be transformed into other forms which present entirely new phenomena.

Notice, for example, the case of the chemical energy of combustion under an ordinary boiler. The heat—a form of

energy — overcomes the cohesion of the liquid water, and steam is produced ; this, by its expansive power in the engine, sets the fly-wheel in motion, and this motion, by means of the dynamo, is converted into an electrical current, which produces heat and light at various points along its circuit.

As has already been pointed out, the connection between heat and chemism is a very close one. In many chemical changes heat is required to bring about the change, while in others heat is given out as a result of the change. In fact, in the production of a chemical compound there is always a definite amount of heat given out or required when the compound is produced under the same conditions.

**Law of Causality.** — All experimental science rests upon another fundamental principle called the law of causality. It is founded on experience. It asserts that every effect (or phenomenon) has a sufficient cause, and, further, that this effect will always follow when the same cause acts under the same conditions.

The three laws just stated are three of the foundation stones upon which the subject of chemistry rests, and the acceptance of their truth by men of science during the last part of the eighteenth century gave to chemistry an impulse and an onward movement that made the present progress of the subject possible.

**Methods and Objects of the Study of Chemistry.** — Chemistry is occupied with a study of phenomena occurring in matter, by which it changes its composition and properties.

The student, therefore, must observe these phenomena, must seek to comprehend them by knowing the conditions under which they are produced. The mere act of observing the changes that occur in matter has very little mental value, unless there is coupled with it an attempt to seek the cause or causes of the changes, and an understanding of how this cause acts, and all the conditions under which it acts.

In studying the elements, therefore, the object sought should be to gain an acquaintance with their physical and chemical properties, the laws that show their relation to each other, and to understand how these facts are built together into the unified body of facts called the science of chemistry.

Each element and its compounds will be studied under the following topics and in substantially the following order : —

1. Occurrence and distribution in nature.
2. Methods of preparation.
3. Preparation.
4. Experimental study.
5. Physical properties.
6. Chemical properties.
7. Name, derivation, meaning, and symbol.
8. History.
9. Uses.
10. Special test for the recognition of the elements.
11. (For compounds.) The determination of molecular formula.

**Method of Experimental Study.** — All experiments should be performed with the following points in the mind of the experimenter, in reference to the order and method of procedure, namely : —

(a) Given certain kinds of matter and energy, what is to be illustrated or proved? For example, given potassium chlorate and sulphur to show that chemical action can be produced by mechanical means, and that the two kinds of matter must be at insensible distances before the action takes place.

(b) To note and determine what are the conditions imposed on the matter. (Describe apparatus and materials used.)

(c) When the student has (a) and (b) well in mind, then should follow the experiment, the careful observation of the same, and the noting the result in a notebook.

(d) Conclusion from the result.

## **HYDROGEN.**

**Occurrence in Nature.** — Owing to the chemical properties of hydrogen, it generally does not exist free in nature. It is found in the gases escaping from some volcanoes. It is, however, widely distributed in nature in combination with other elements. It occurs as an essential constituent of animal and vegetable compounds, in water, and in all acids. It constitutes nearly one-ninth of the weight of water. It is found in volcanic gases, in meteors, in gases that escape from oil-wells, and in the so-called natural gas. It is also found in the sun, fixed stars, and nebulae.

**Preparation.** — Since hydrogen occurs only in chemical compounds, it must be separated before it can be studied as an element. It can be separated from its compounds in many ways; however, only two methods will be referred to now: —

1. By electrolysis.
2. By the action of acids on metals.

**First Method.** — Attention has been called in the introduction to the mutual convertibility of electrical and chemical energy. The action in the battery producing the current is chemical. Now when this electric current acts on water under the proper conditions, it separates it into two substances, one of which will be found to have the properties of hydrogen. This method of preparation will be practically studied when the subject of water is considered.

**Second Method.** — Place in a generating-bottle 20 g. of zinc, and pour down the thistle-tube 30 to 40 cc. of dilute sulphuric

acid, 1 vol. of acid to 4 vols. of water. (Add the acid to the water in diluting.) Collect the gas over water. Reject the first gas that escapes; that is, a volume equal to two or three times the volume of air in the generating-bottle and collecting-tubes. Save the contents of the generator, and filter; if the solution is not clear, allow the water to slowly evaporate, and examine the residue. Where is the zinc? After collecting a sufficient number of bottles<sup>1</sup> of gas, make the following study of the gas, noticing carefully all the points given in the introduction, page 24.

**Experimental Study, No. 3.** — (a) As a preliminary test remove a bottle of gas from the trough, keeping the mouth downward and covered. (Pieces of smooth, thin quarter-inch board, 8 cm. square, make good covers.) Light a splinter of pine wood (20 to 30 cm. long), remove the cover from the bottle, and bring it in contact with the gas. Plunge the stick up into the gas. What takes place at the mouth of the bottle? These results are characteristic of this gaseous body called hydrogen.

(b) Take a bottle filled with air, and a bottle of the gas, and place them mouth to mouth with the hydrogen bottle uppermost. (The finger clasping the necks may serve as a seal.) Keeping the bottles tightly together, invert them, with the bottle containing the air coming uppermost. Examine carefully for any changes. What are the new conditions? Permit the bottles to remain in this position one minute. Test each jar with a burning stick, as in the preliminary examination (a). What inference can you draw from these results as to the mass of the gas when compared with air? Test a jar of pure air with a burning stick. The same property may be shown by blowing soap-bubbles with the gas.

(c) Remove a bottle of gas from the trough, keeping the

<sup>1</sup> Six- and twelve-oz. salt-mouth bottles afford excellent collecting-jars, and cost but little. This will be the gas-bottle referred to hereafter.

mouth covered and downward. Bring a lighted stick near the mouth of the bottle. Plunge it up into the bottle and then withdraw it. Repeat it until the result is understood. Describe the conditions of the experiment, especially the conditions at the mouth of the bottle. What is shown when the burning of the stick ceases on being placed in the gas? Explain why the action continues at the mouth of the bottle. What matter enters into the action?

(*d*) Fill a bottle  $\frac{3}{4}$  full of water and invert it in the trough, thus leaving it  $\frac{1}{4}$  full of air. Displace the water with hydrogen. Remove the bottle from the trough and cover it with a towel; remove the cover and bring a burning stick to the mouth of the jar. What is the evidence of chemical change? Why were you directed to throw away the first bottle of gas?

(*e*) After a few bottles of gas have been collected, wipe the jet and ignite the escaping gas. (The gas should escape rapidly when it is ignited.) What is the flame? Hold over the burning jet a cold beaker. What appears to be the product? Hold in the flame a piece of platinum wire. What inference may we draw as to the temperature of the flame?

(*f*) Fit up a piece of apparatus, as shown in Fig. 1. The jar *a* is the clay cylinder used in a Daniel battery cell. It is placed mouth downwards, and is closed tightly by a rubber stopper or by a paraffined cork *b*. *c* is a small glass tube about 50 cm. long. The beaker *d* is

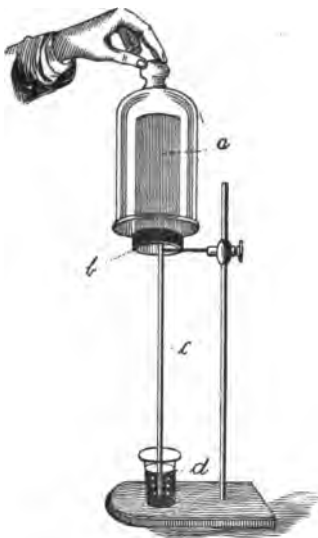


FIG. 1.



partly filled with some colored solution ; *e.g.* magenta or permanganate of potassium, etc. The end of the glass tube *c* dips under the colored solution. Note the conditions. What is in the interior of the jar? Is it connected with the outside air? Now bring a jar containing hydrogen over the cylinder. What new conditions are imposed? Notice what follows. What can cause the gas to escape? Can it be due to increasing temperature? Why not? Remove the jar from the cylinder. What can cause the liquid to rise in the tube? Repeat until the facts are clearly seen. How could you prove that there is hydrogen in the clay cylinder?

The following inferences may be drawn from the facts discovered : —

(1) That the hydrogen must have passed through the cylinder, and if the air passed out at all through the cylinder it must have done so more slowly than the hydrogen passed in ; hence the increased pressure on the inside of the cylinder, or the accumulation of gas in the cylinder, and its consequent escape at the place of least resistance.

(2) When the jar was removed, the more rapid movement of hydrogen gas produced the opposite effect upon the cylinder ; that is, the pressure was reduced and the liquid arose in the tube.

(3) May we not also conclude that the gas is not a continuous mass, but that it must be divided into small particles in order to pass through the cylinder? Again, that these particles of hydrogen move faster than particles of air?

(*g*) Fit up the generating apparatus for preparing hydrogen, using sufficient material to prepare the gas quite rapidly. (A piece of platinum foil in contact with the zinc in the generator increases the rapidity of the formation of hydrogen.) Insert a metallic jet in the end of the conducting-tube and permit sufficient gas to escape to render it safe to light it. Have ready a platinum sponge and a piece of platinum foil (or palladium)

which has recently been heated to redness and cooled. Now place the sponge in the escaping hydrogen. Make the same examination with the foil and the palladium. What elements are present? What is the evidence of the chemical action? These metals have the property of absorbing gases upon their surfaces. In what condition must hydrogen and oxygen be on the surface? (Platinum sponge is different from the foil, since it is very finely divided.) What effect will that have on the amount of surface of a given weight of platinum?

Doebereiner's lamp is made on this principle. It consists of a large jar in which dilute sulphuric acid is placed. Suspended in this is another jar, open at the bottom, and closed at the top with a stop-cock. In this inner jar is suspended a mass of zinc. When the stop-cock is open, the dilute acid rises in the inner jar, comes in contact with the zinc, and hydrogen is generated. When the stop-cock is closed, the hydrogen that is generated depresses the liquid until it entirely leaves the zinc. The gas, therefore, is under some pressure when not in use. The gas escapes through a fine jet against a platinum sponge, when it is soon ignited by the heat produced. The lamp was very useful, before the invention of matches, for starting fires.

**Physical Properties.** — From the examination of hydrogen, in connection with the more careful work in the same direction by others, the following physical properties can be stated: Hydrogen is a gas, colorless, tasteless, and odorless. If it had been examined by the sense of hearing, it would be found to transmit sound readily and with greater velocity than the air, and to change the quality of the tone produced in its midst. It is lighter than air; in fact, it is the lightest known substance. A litre of the gas under standard conditions (that is,  $0^{\circ}$  temperature, and under a pressure of 760 mm.), has a mass of .0896 g. The exact mass is .089578 g. This number should be remembered, since in this work the specific gravity or vapor density of all gases is referred to it as the standard.

Careful experiments show that 1 l. of water, under standard conditions, will absorb .0193 l. of hydrogen. When subjected to pressure and a low temperature, all gases can be changed to liquids and sometimes to solids. Until 1877 hydrogen had resisted all attempts to change its form. In that year MM. Pictet and Cailletet, by subjecting the gas to a pressure of 650 atmospheres and a temperature of  $-140^{\circ}$ , converted it into a steel-blue liquid. When the space in which the hydrogen was included was opened to the air, a portion of the liquid was solidified by means of the lowering of the temperature due to the rapid evaporation of the liquid.

Hydrogen diffuses readily in unglazed earthen vessels at ordinary temperatures. At high temperatures—red heat—it passes through many metals. This latter statement is true of many other gases; *e.g.* carbon monoxide. The rate of diffusion of gases has been found to vary inversely as the square root of their densities. This is the law of Graham. Therefore the rates of diffusion of hydrogen and air are approximately as 1 : 4. The density of the air is 14.43. If we compare the rate of diffusion of hydrogen with oxygen, one of the constituents of air whose density is 16, the rate is more nearly in the ratio of 1 : 4. The facts may be expressed mathematically thus :—

$$\text{Rate of O : rate of H} :: \sqrt{1} : \sqrt{16}, \text{ or as } 1 : 4.$$

Several metals, notably platinum and palladium, have the property of absorbing hydrogen in relatively large quantities. Platinum will absorb 3.8 times its own volume at red heat. The volume of the platinum is also increased. Palladium has this property of absorbing hydrogen in the highest degree. At red heat it absorbs 935 times its own volume. The palladium becomes lighter, volume for volume, and assumes other new properties. Many other substances possess this power of absorbing gases on their surfaces, but to so slight a degree that it is not ordinarily noticed.

**Chemical Properties.** — It will be noticed in the experimental study of hydrogen that at ordinary temperatures it does not unite with the air, but that it requires red heat to start the action. This is generally true of the element in its chemical relations to other elements. It does not unite at ordinary temperatures with other elements. This will be illustrated when its compounds are studied later on. When the gas “burns” in the air, it produces an almost invisible flame, if the gas is pure and is burned at a metallic jet. The product of the burning is water.

**Tests for Hydrogen.** — As we have seen, a body is recognized by its chemical and physical properties. A test, therefore, must include a study either of these properties as a whole or of some of the properties that are characteristic. It is not often that a single property will suffice to identify a body. Another idea is also included in a test. It means—*e.g.* in case of hydrogen—that we know how hydrogen itself acts under given conditions. Now if a given body acts in the same way under the same conditions as a known body acts, we can assert that the two bodies are identical. Hydrogen can therefore be recognized by the flame test, in connection with its other physical and chemical properties. If compared with other substances, it will be found that it stands out as an individual substance, and therefore is an element.

**Name, Derivation and Meaning; Symbol.** — The word *hydrogen* is formed from two Greek words meaning water and I form (or generate), and consequently means, I form or generate water. The name was given to it by Lavoisier, because it was found to produce water when burned in the air. The symbol is H.

**History.** — Paracelsus, in the sixteenth century, noticed that when certain metals were acted upon by an acid a gas escaped, and that it was inflammable when heated in air. He called it “an air”; and because of this property of inflammability, he

named it an inflammable air. In 1766 Cavendish showed that hydrogen is a distinct substance, and in 1781 he proved that water is formed by the union of two gases, oxygen and "inflammable air" or hydrogen. Lavoisier also proved that hydrogen is a constituent of water.

**Uses.** — The great lightness of hydrogen makes it useful for filling balloons, it being 14.43 lighter than air. Its specific gravity on the air scale is .0693. Its uses in the oxy-hydrogen blow-pipe and in the calcium light will be described later on.

---

## CHLORINE.

**Occurrence in Nature.** — The chemical character of chlorine prevents its occurrence in nature as a free substance. It is, however, widely distributed in combination. It is found in large quantities, combined principally with the metals sodium and potassium. The former compound is called common salt, or rock salt. It exists in this form in sea-water, in many springs, and in vast deposits.

**Methods of Preparation.** — Common salt is the chief source of chlorine. The salt is either used without change, or first a compound of hydrogen and chlorine is prepared, and from this the chlorine is set free. There are two methods commonly employed in the preparation of chlorine. In the first method hydrochloric acid is heated with manganese dioxide; and by the second method common salt and manganese dioxide, sulphuric acid, and water are heated together.

Chlorine is also prepared from hydrochloric acid by the action of the electric current. This will be described when the acid is studied.

**Preparation.** — Use an Erlenmeyer flask of about 300 cc. capacity, fitted up in the same manner as the generating-bottle

previously described, or the safety-tube may be omitted. Place in the flask 10 g. of dioxide of manganese, and add 35 cc. of concentrated hydrochloric acid. (For every litre of chlorine about 10 g. of manganese dioxide are required and 35 cc. of hydrochloric acid, specific gravity 1.16.) Heat slowly. Fill six to eight dry gas-bottles with gas, by downward displacement, keeping the bottles covered tightly.

If the second method of preparation is used, proceed as follows: Use equal weights of common salt and of manganese dioxide, say 10 g. of each. Mix thoroughly in a mortar. Place in a flask, arranged as in the preceding method, and add sufficient sulphuric acid to cover the mixture. Heat carefully, and collect the gas as before.

Chlorine is made from bleaching-powder by putting 30 g. of it in a generating-flask fitted for collecting gases, and pouring on it concentrated hydrochloric acid.

**Experimental Study, No. 4.** — (a) Examine for physical properties, such as color, odor, taste, specific gravity, and state of aggregation.

(b) Solubility in water. Use a bottle of the gas, adding 50 cc. of water. Close tightly with a solid rubber stopper and shake thoroughly. Place the mouth of the bottle under water and remove the stopper. Explain the result. What has become of the chlorine?

(c) Show the chemical relation to air at ordinary temperatures and at raised temperatures. (The latter is always done in one way; that is, by a burning stick or candle.) The stick should always be brought to the mouth of the bottle, noting each time the actual conditions. Then it should be plunged into the gas. What inference can be drawn from this experiment?

(d) Generate hydrogen until it is safe to ignite it and place the jet in another bottle of chlorine gas. Place a piece of blue litmus paper in the bottle near the jet. Pour 10 cc. of water

into the bottle ; close and shake. Taste of the solution and test with blue litmus paper. What is the taste? Note the effect on the litmus paper. This is the effect produced by a class of substances called acids.

(e) In another bottle of gas introduce a strip of blotting-paper moistened with hot turpentine. Test the jar with blue litmus paper after the reaction. (The action is more certain if the chlorine has been dried by passing it through sulphuric acid.) What is the black substance left? (Turpentine contains carbon and hydrogen.)

(f) With a deflagrating-spoon lower a piece of phosphorus into the jar, the phosphorus being at ordinary temperature. Ignite the phosphorus and lower it into the gas. To what is the difference in action due? Of what must the product consist?

(g) Place a piece of Dutch metal in the gas. What is Dutch metal?

(h) Place a strip of dry calico in a bottle of dry gas. Allow it to remain in the gas for a few minutes. Now moisten with water and return to the same bottle. What does the bleaching mean from the chemical standpoint?

(i) Chlorine gas passed through water is called chlorine water. Treat 60 cc. of such a solution in a test-tube with a few drops of silver nitrate solution. Make note of the result for future reference.

(j) Expose a test-tube full of the chlorine water to bright sunlight ; that is, invert the tube in a small dish (say, a three-inch evaporating-dish) containing enough chlorine water to cover the mouth of the tube. Allow it to stand in the sunlight for two hours. Close the tube, invert it, and bring the coal of a burning match into the gas. This fact should be studied again under the subject WATER. Allow a tube thus prepared to stand until the color disappears. Is there any free chlorine present? Give reason for your decision. Test the solution

with blue litmus paper. Note the result for future use. Taste the solution. To 5 cc. add a few drops of silver nitrate. Compare the result with (i).

(k) Cut a piece of sodium as large as a pea, place in the spoon, and lower into the gas. When the action is complete, compare the product with common salt; *e.g.* taste it.

(l) Bring the bottle containing ammonia water near the mouth of a bottle of gas. Note and describe the result.

**Physical Properties.** — An examination of chlorine has shown that it is a gas heavier than air, greenish yellow in color, possessing a suffocating, irritating odor, and an unpleasant taste. It is soluble in water, 1 l. of which at 1° dissolves 3 l. of chlorine gas. When its saturated water solution is cooled to 0° and below, a crystalline body separates out, which is found to consist of chlorine and water. It is heavier than air, as is shown by the method of collection of the gas. One litre of it weighs 35.37 times as much as a litre of hydrogen; that is, its vapor density is 35.37. When inhaled, it acts like an irritating poison, causing inflammation of the mucous membrane and producing a sensation in the head like a cold. It is changed to a yellow liquid at 0° and under pressure of six atmospheres. The liquid boils at -33.6.

**Chemical Properties.** — From the experiments made with chlorine it can be inferred that it is, chemically speaking, a very active element, even at ordinary temperatures. It combines not only with copper and zinc, but with nearly all metals forming stable compounds. It unites with hydrogen to form a gaseous compound which changes blue litmus paper to red. If equal volumes of chlorine and hydrogen are mixed and exposed to the direct sunlight, they unite with great energy. In diffused sunlight the union takes place gradually, while in the dark no chemical change occurs. The affinity of chlorine for hydrogen is so great that it will remove it from any of its compounds, as in the case of turpentine ( $C_{10}H_{16}$ ). Most coloring-matters con-



tain carbon and hydrogen; and the removal of the hydrogen destroys the compound, producing, often, colorless ones, as in the case of the calico. In most cases, especially where moisture is necessary, it is probable that oxygen is set free from the water and that it does the bleaching. (See under OXYGEN.)

**Name, Derivation, and Symbols.** — The name chlorine was given to this element by Davy in 1810. He so named it because of its greenish yellow color. The word *chlorine* is derived from the Greek word *chloros*. The symbol is Cl.

**History.** — To the Swedish chemist Scheele must be given the credit of discovering this element. In the year 1774 he prepared it from manganese dioxide and hydrogen chloride, then called muriatic acid. The product was called by Scheele "dephlogisticated marine air." It was not regarded by him as an element, and was later thought to contain oxygen. Some writers considered it a compound of muriatic acid and oxygen. In 1810 Sir H. Davy determined its elemental character.

**Uses.** — Its uses are principally as a bleaching agent and a disinfectant, antiseptic, and deodorizer.

**Tests.** — The free chlorine gas is easily detected by its physical properties. Such chemical properties as its bleaching action on vegetable colors, its white fumes with ammonia gas, serve as a means of detecting and recognizing the element.

---

## BROMINE.

**Occurrence in Nature.** — Like chlorine, in many of its properties, bromine is not found free in nature. Sea-water contains not only common salt, — that is, the elements chlorine and sodium combined, — but it contains sodium and bromine combined, or sodium bromide. It is therefore widely distributed, but the amount in sea-water is very small. In the Dead Sea

there is said to be as much as .42 g. per litre. It is found in many spring waters in America and Europe; *e.g.* in the spring at Kreutznach and in Ohio. It is also found in potash salt deposits at Stassfurt, Germany, and combined with silver in Mexico.

**Methods of Preparation.** — Bromine is prepared from its compounds with sodium or potassium by methods similar to those used in preparing chlorine. It may also be prepared by treating a solution of a bromide with free chlorine, or with chlorine water. The method most commonly used is that in which dioxide of manganese, sodium bromide, and sulphuric acid are heated together, or the method in which the bromine is set free by means of chlorine gas.

**Preparation.** — *Material:* 20 g. dioxide of manganese, 25 g. sodium or potassium bromide, and about 70 cc. of sulphuric acid diluted with 50 cc. of water. (Always pour acid into the water in mixing.) *Apparatus:* A 300 cc. flask and an ordinary condenser, or a long glass tube, the end of which should dip under water. The flask should also be provided with a safety-tube.

The material is placed in the flask, the solids being first thoroughly mixed, the connections made, and the flask gently warmed. The bromine will collect at the bottom of the receiver after the water becomes saturated. Care should be taken in experimenting with bromine, since it is injurious to inhale it or bring it in contact with the skin.

**Experimental Study, No. 5.** — With the bromine prepared by the methods just described, or with some from the laboratory supply, make the following examination of its physical and chemical properties: —

(a) Put a few drops in a dry gas-bottle, cover, and shake. Open, and incline as you would to pour water from the bottle. Examine for color and odor.

(b) In another bottle put two drops of bromine, add 30 cc.

of water ; cover and shake. Take 10 cc. of this solution in a test-tube, add 2 cc. of bisulphide of carbon, and shake vigorously. Note the color of the bisulphide after it has settled out.

(c) Examine other bottles of gas prepared like (a), according to methods given under CHLORINE, from (e) to (l) inclusive. Describe results.

**Physical Properties.** — At ordinary temperatures bromine is a reddish brown liquid, and is the only element except mercury that exists as a liquid at such temperatures. When exposed to the air it readily passes into reddish brown vapor. As a vapor it has an intensely disagreeable odor, attacking the mucous membrane, and producing marked irritation. It particularly attacks the eyes. Its density is 79.75. It is slightly soluble in water and readily so in carbon disulphide, producing a yellow to reddish-yellow solution, depending on the quantity dissolved. This water solution is called bromine water.

**Chemical Properties.** — In its chemical properties bromine is very like chlorine. It combines with the metals readily. It does not combine with hydrogen at ordinary temperatures nor in the sunlight, but if the vapor is heated with hydrogen a small amount of the compound is formed. It unites with phosphorus, with the evolution of considerable heat. It bleaches organic compounds readily, although not so readily as chlorine. It decomposes water like chlorine.

**Name and History.** — The name of the element was applied to it by Balard in 1826. He found it in the mother liquor from common salt works, especially those using sea-water. The word signifies a stench and at once points out its marked property. The symbol is Br.

**Uses.** — Bromine is used as a disinfectant and antiseptic, also in the preparation of a large number of compounds, and in laboratory investigation. It is used in medicine and in photography. The amount produced annually is not far from 300,000 kilos. Its production is a recent industry ; and as

late as 1865 it was prepared in small quantities only, and was used mostly as samples in teaching chemistry. The price then was about \$16 per pound, while to-day it costs not far from 25 cents per pound.

**Tests.** — Free bromine is recognized by its odor and color and by its action on carbon disulphide when in water solution. When its water solution is shaken with ether or chloroform, characteristically colored solutions are produced.

---

## IODINE.

**Occurrence in Nature.**— Iodine does not occur in nature as a free element, its chemism causing it always to unite with some other element. Its compounds occur in small quantities in sea-water, and in the bodies of both animals and plants living in sea-water; *e.g.* in sponges, the livers of certain fishes, in oysters, and in sea-weed. It is always found in Chili salt-petre, combined with silver in Mexico, and in sea-water. Sea-weed is one of its principal sources.

**Methods of Preparation.** — In the preparation of any substance for commercial purposes, the cost of manufacture decides the source from which the crude material shall come and the process by which it shall be prepared, providing there are several sources from which it may be procured.

Various kinds of sea-plants assimilate the compounds containing iodine, thus virtually condensing the sea-water, so far as this substance is concerned. The gathering and burning of the weeds, after the storms have thrown them on the shore, forms the occupation of a large number of persons living on the coast of Ireland and Scotland and France. In the early part of this century the ashes of these sea-weeds sold for about \$100 per ton; but owing to the discovery of iodine in Chili

saltpetre, this method for its production has been quite largely superseded. The deeper-sea varieties of plants, like the fucus, yield a larger amount of iodine, and it is said that these weeds are farmed and collected at the proper season. The weeds are burned in such a way that the temperature shall not become high enough to decompose any of the compounds of the iodine. At present the weeds are merely carbonized. The residue (called kelp) is washed to remove the soluble parts, and the solution thus made is evaporated to dryness. One ton of kelp will produce from 5 to 10 k. of iodine. The compounds of iodine and bromine (of the latter there is only a small amount), being more soluble than the other compounds found in the ashes, are left in solution, while the others crystallize out. The iodine is now set free either by treating the residue with sulphuric acid and manganese dioxide or by passing chlorine gas through the solution. The iodine is driven into cooling chambers, where it solidifies.

**Experimental Study, No. 6.** — Iodine can be prepared from its compound (potassium iodide) according to the treatment just given, but it is usual to furnish the student with the element already free.

(a) Leave a small piece of iodine exposed to the air for several hours. Note the changes that have taken place. What physical property is thus discovered?

(b) Place two or three small pieces of iodine in a test-tube and warm gently. Incline the tube as if to pour from it. What does the result indicate? Determine the odor.

(c) Pour 10 cc. of water into a test-tube containing a crystal of iodine and shake well. Warm and set aside for further examination.

(d) Use alcohol in place of water. Compare with (c).

(e) Pour 2 cc. of bisulphide of carbon into the water solution of (c) and shake. Allow it to stand, and examine liquid at the bottom of the tube. What is it? To what is the color due?

(*f*) Dip a piece of litmus paper in a water solution of iodine and compare the result with that produced when bromine or chlorine solutions were used. Allow the litmus paper to remain in the iodine solution for an hour or more, and then expose it to the air. Note the changes.

(*g*) Make a starch paste by rubbing a few pieces of starch in water and then bringing the water to a boiling point. To 10 cc. of water add 1 cc. of the starch solution and a few drops of the solution of iodine in alcohol. Shake well.

(*h*) Dissolve a crystal of potassium iodide in water, add bisulphide of carbon and shake. Now add a few drops of chlorine water. Compare with (*c*).

(*i*) Produce the vapor of iodine in a gas-bottle or test-tube, and test by a burning stick.

(*j*) Rub a crystal of iodine in a mortar with mercury, adding 2 cc. of alcohol. What becomes of the mercury?

(*k*) Lay two or three crystals of iodine on a bit of freshly cut phosphorus. Use the plate of the retort-stand.

(*l*) Heat in a test-tube a mixture of iodine and sulphur, the mixture being covered with water. Note carefully the evidence of chemical change from (*i*) to (*l*), inclusive.

**Physical Properties.** — An examination of the element iodine shows that it possesses the following physical properties: It is a solid, occurring usually in blackish gray scales, which are crystalline in structure. When left exposed to the air at ordinary temperatures it slowly vaporizes, but at higher temperatures it is rapidly converted into a heavy blue vapor. When this vapor is mixed with air, it has a violet color. Its vapor density is 126.54. It has a peculiar taste and a penetrating odor, but, however, it is less penetrating than chlorine or bromine. It is slightly soluble in water, but is readily so in alcohol, carbon disulphide, chloroform, and other liquids.

**Chemical Properties.** — Iodine has but slight bleaching effects on litmus, and with a starch solution free iodine forms a char-

acteristic blue compound. It is freed from many of its compounds by chlorine. It unites readily with many metals and non-metals; *e.g.* mercury, phosphorus, and sulphur. It does not unite with hydrogen at ordinary temperatures.

**Tests.** — Free iodine in water solution is recognized by its action either on bisulphide of carbon or on chloroform. It produces a deep violet-colored solution with a starch solution. As an element, its physical properties are sufficiently characteristic to distinguish it from other substances.

**Name and History.** — Iodine was accidentally discovered in 1811 in the kelp of sea-weeds by Courtois, its color directing his attention to it. The name signifies violet-colored. Three years after its discovery Guy-Lussac determined its elementary character.

**Uses.** — Iodine is commercially quite important. Its compounds are used largely in photography, in medicine, dyeing, and in chemical research. Over 100,000 kilos are used annually.

---

## FLUORINE.

**Occurrence in Nature.** — Fluorine is widely distributed in nature, although always in combination with other elements. Its principal natural compounds are the minerals fluor-spar and cryolite. The former is found in the United States in New York and New Hampshire, and in England. In England it is found in large quantities at Derbyshire, where it is cut and polished for vases and ornamental figures. Cryolite (literally, ice-stone) is found in great abundance in Greenland. It contains sodium, fluorine, and aluminium. Fluorine is also found in sea-water and in the teeth and bones of mammals.

**Preparation.** — The chemical character of fluorine prevents its easy preparation; in fact, until the year 1886 it had never

been freed from its compounds. Moissan, by preparing a pure compound of hydrogen and fluorine and subjecting it to the action of electric sparks, succeeded in setting the element free.

**Physical Properties.** — Fluorine is a colorless gas having a probable density of 19. Its other physical properties are not yet well known.

**Chemical Properties.** — Fluorine exhibits strong chemism towards nearly every element, oxygen and platinum being excepted. Its union with hydrogen occurs even in the cold, accompanied with violent explosions. Metals unite readily with it, the action being accompanied by heat and light. Instead of being soluble in water it decomposes it, taking its hydrogen and setting oxygen free.

**Name and History.** — The word *fluorine* is derived from the name of the mineral, fluor-spar. This name was applied to the spar because it fuses when heated, and also because it is used as a flux in fusion processes, the word *flux* signifying to flow. The element was freed in 1886 by Moissan, although its existence was known long before this time, but it had resisted all previous attempts to set it free. The element, therefore, cannot be said to have any uses, although some of its compounds have been in use for a long time. Its symbol is F or Fl.

*A Study of the Chemical Relations among Chlorine, Bromine, and Iodine, as shown by a Study of their Compounds with Other Elements.*

**Material.** — Compounds of bromine and iodine with each potassium and sodium, chlorine and bromine water, and bisulphide of carbon.

**Preparation of Material.** — A crystal of each compound is dissolved separately in 25 cc. of water.

**Experimental Study, No. 7.** — (a) Treat 5 cc. of each solu-



tion with carbon disulphide ; shake well, and set aside for comparison with (b), etc.

(b) Treat 10 cc. of each solution with 5 cc. of chlorine water, then with 2 cc. of bisulphide of carbon ; close the tube, and shake vigorously. Set this aside for further examination. Compare with (a).

(c) Treat 10 cc. of the solution containing the iodine compound with a little bromine water and warm gently. Cool, and test with bisulphide of carbon. Note result.

(d) Mix 10 cc. of each of the solutions containing iodine and bromine compounds, and to one-half the mixture add chlorine water and test with bisulphide of carbon. Take the other 10 cc. and treat with much chlorine water, and boil. Notice whether the color of the solution changes. When it becomes light yellow, cool and test as before. What has become of the iodine? Did it escape as a gas? Treat a portion of the solution with sulphur dioxide. (See under SULPHUR DIOXIDE for method of preparation.)

**Conclusions from this Study.** — 1. That chlorine is stronger chemically than either iodine or bromine. Explain this.

2. That bromine is stronger chemically than iodine.

3. That chlorine sets iodine free first, in a mixture containing compounds of both iodine and bromine.

4. That chlorine not only sets iodine free, but causes it to enter into new combinations which are colorless.

*Compounds of Hydrogen with Each Chlorine, Bromine, Iodine, and Fluorine.*

(A) HYDROGEN CHLORIDE.

**Occurrence in Nature.** — This compound occurs in the gases escaping from volcanoes and also in the waters of some of the rivers of South America.

**Methods of Preparation.** — While studying chlorine it was noticed that hydrogen unites with it with great rapidity, often causing explosions when the temperature of the mixture of the two gases is only slightly raised ; that a mixture of the two gases unites slowly in diffused light and quickly in bright sunlight.

For experimental purposes it is usually prepared from common salt and sulphuric acid.

**Preparation.** — Place 25 g. of common salt in a 300 cc. Erlenmeyer flask (hereafter called an E. flask), and prepare for the collecting of gas by downward displacement. Add 40 cc. of concentrated sulphuric acid and warm sufficiently to cause the gas to flow as rapidly as desired. Collect a sufficient number of bottles of gas for the experimental study. (The gas may be passed into water until the bubbles are wholly absorbed before collecting in bottles. Cover the bottles tightly.) When sufficient gas has been collected, continue to pass the gas into water for some time. Save this last product for further examination.

**Experimental Study, No. 8.** — (a) Examine for physical properties, as described under CHLORINE. Specific gravity can be determined qualitatively by placing ammonium hydroxide in an open dish and inclining over it a bottle of the gas as if to pour it out. To a bottle of the gas add 30 cc. of water ; close tightly, shake, and open with mouth under water.

(b) Test the gas with moist blue litmus paper.

(c) Test another bottle of the gas with a burning stick. This proves what?

(d) Ignite sulphur in the iron spoon and plunge it into the gas. Examine the contents of the bottle.

(e) While the gas is escaping bring the open ammonia bottle near the jet. What is the evidence of chemical change?

(f) Place a small bit of sodium in a spoon, lower it into the dry gas, and leave for some time. Examine the residue in the spoon. Taste it. What substance does it resemble in taste?

(g) Warm a piece of magnesium and plunge it into the dry gas. Ignite the magnesium and plunge into the gas, keeping the bottle covered. Examine the product. Bring a burning match near the mouth of the bottle. What substance is indicated?

(h) Add 10 cc. of silver nitrate solution to the solution of the gas in water. Expose the product to the direct sunlight.

(i) Boil 10 cc. of the water solution of the gas and test the escaping steam with litmus paper. Continue the boiling until nearly all the water has escaped, and then test the remainder with litmus paper. Taste of it. What inferences can you draw from these results?

(j) Place a piece of magnesium ribbon in a test-tube and add some of the water solution of the gas. Collect the escaping gas in test-tube and determine what it is. Where is the magnesium? Evaporate solution to dryness. What is the source of the gas? Does the water give the gas? What elements does the compound contain?

**Physical Properties.** — The compound is a gas at ordinary temperatures and pressure. It is colorless and possesses an irritating odor and a sour taste, or it is an *acid*. That it is heavier than air is seen by the manner of collecting it. It is 18.18 times heavier than hydrogen. It can be changed to a liquid by pressure of 40 atmospheres and at a temperature of  $10^{\circ}$ . It is very soluble in water; so soluble that 1 vol. of water (e.g. 1 l.) takes up 500 vols. of the gas at  $0^{\circ}$ , and 450 vols. at ordinary temperatures. When a saturated solution of the gas is heated, it is given off at first with but a small amount of water vapor. The temperature, however, soon rises to  $110^{\circ}$ , and the distillate contains both the acid and water, 20 per cent of the former and 80 per cent of the latter. Pressure modifies these proportions; the lower the pressure, the more of the gas escapes. The solution of this compound is commonly called hydrochloric acid, or, commercially speaking, muriatic acid.

It is also called hydrogen chloride, although the latter name should be applied to the gas only.

**Chemical Properties.** — Hydrogen chloride possesses in general the same properties in solution that it does as a gas. It changes blue litmus paper to red, one of the characteristic properties of the inorganic compounds called acids. It does not aid in ordinary burning and does not react with the air. In its water solution it attacks metals, such as zinc and magnesium, and hydrogen is set free. Magnesium and sodium decompose the gas and form solid compounds with the chlorine, setting hydrogen free.

**Name and History.** — The name *hydrochloric acid* (or *hydrogen chloride*) signifies a compound of hydrogen and chlorine, and that such a compound is acid. (See under NOMENCLATURE.) (The name hydrochloric acid will be used to refer to the water solution of hydrogen chloride, and thus distinguish the two from each other. The same method of distinguishing gaseous acids from their water solutions will be used hereafter.) The acid was prepared by Basil Valentine in the fifteenth century, although a mixture of its water solution with nitric acid was made much earlier. It was not known as a gas until Priestly collected it over mercury in the year 1772. In 1810 Davy showed that it is composed of hydrogen and chlorine.

**Uses.** — Hydrochloric acid is used under two designations; *i.e.* as chemically pure (or C. P.) and commercial acid. The commercial acid is used extensively in manufacturing processes. The chemically pure compound is used in analytical chemistry. It is used in water solutions containing from 25 to 40 per cent of the gas.

**Tests.** — This acid in solution is tested for by means of a solution of silver nitrate. The compound formed is not soluble in nitric acid and turns black when exposed to the light.

**(B) HYDROGEN BROMIDE.**

**Methods of Preparation.** — Hydrogen bromide cannot be made by bringing hydrogen and bromine together at ordinary temperatures, as was seen when studying bromine. It can be prepared by the following methods: —

(a) By passing the mixture of hydrogen and bromine vapor over a hot platinum sponge, the sponge acting as it did in the experiment with hydrogen. (See page 28.)

(b) By treating the compounds of phosphorus and bromine with water. The water is decomposed, the bromine taking a part of the hydrogen, and the phosphorus taking the remainder of the hydrogen and the oxygen.

(c) By the action of phosphoric acid on the compound of potassium and bromine.

**Preparation.** — Fit up the apparatus as is shown in Fig. 2. Place in the flask 3 g. of red phosphorus (not the common

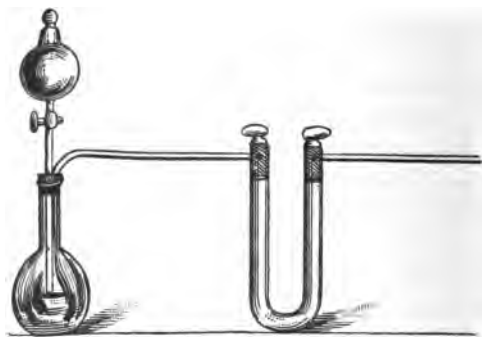


FIG. 2.

yellow phosphorus) and 10 cc. of water. Next place 30 g. of bromine in the separating funnel and allow it to drop slowly into the mixture of phosphorus and water. There follows a rapid evolution of gas which can be collected by downward

displacement, or it can be passed into water and water solution prepared. The gas should be passed through a tube containing red phosphorus, to free it from any free bromine.

**Experimental Study, No. 9.** — This gas should be now examined to determine its physical and chemical properties; *e.g.* color, taste, odor, and solubility, following the directions given under CHLORINE.

(a) Pour 5 cc. of chlorine water into a bottle of the gas and shake, or pass chlorine gas into a bottle of the gas. Test the solution with bisulphide of carbon.

(b) Examine another bottle of the gas with moistened litmus paper. For other experimental study, follow the directions given in Experimental Study, No. 8. Study especially (f) under No. 8.

**Physical Properties.** — Hydrogen bromide is a colorless gas, possessing an irritating odor. It has such an attraction for water that the gas fumes in ordinary air; that is, water is condensed from the moisture in the air. It is a heavy gas, having a density of 40.38. It can be converted into a liquid and finally into a solid by the usual means, — increase of pressure and reduction of temperature. It is readily soluble in water, the solution being acid to taste and to litmus paper. The saturated water solution at 0° contains 82 per cent of acid.

**Chemical Properties.** — Hydrogen bromide is very like the corresponding compound of chlorine in its chemical character. The bromine is set free by chlorine, showing that its chemism for hydrogen is less than that of chlorine for hydrogen.

**Uses.** — It is used in medicine in its water solution.

### (C) HYDROGEN IODIDE.

**Methods of Preparation.** — This compound rarely exists free in nature, but can be formed by processes similar to those given for preparing hydrogen bromide: —

(a) By passing a mixture of hydrogen and iodine vapor over a hot platinum sponge.

(b) By treating a compound of phosphorus and iodine with water.

(c) By the action of phosphoric acid on a compound of potassium and iodine.

**Preparation.** — Fit up the apparatus, as shown in Fig. 2, and proceed as in preparing the compound of hydrogen and bromine, except that the iodine and phosphorus are placed together in the flask and warmed gently until action ceases. The water is then added, drop by drop.

**Experimental Study, No. 10.** — Examine the gas in the same manner that the hydrogen bromide was examined. If the gas contains free iodine, it may be removed by passing it over red phosphorus contained in a U-tube.

**Physical Properties.** — This compound is a colorless gas of an unpleasant and suffocating odor. Its water solution is acid to the taste and to litmus paper. It fumes in the air and is a very heavy gas, having a density of 63.27. It can be changed to a liquid and to a solid. It is very soluble in water, and the saturated water solution at 0° has a specific gravity of 1.99 and contains more than 75 per cent of acid.

**Chemical Properties.** — Chemically speaking, hydrogen iodide is a very unstable compound. Its water solution decomposes in the sunlight, the iodine being set free. At 180° heat alone decomposes it into hydrogen and iodine. Chlorine or bromine gas when mixed with it sets the iodine free. Metals decompose the compound, setting hydrogen free, and unite with the iodine.

#### (D) HYDROGEN FLUORIDE.

**Methods of Preparation.** — Hydrogen fluoride is prepared from one of the natural compounds containing fluorine, fluor-spar, by the action of sulphuric acid on the compound.

**Experimental Study, No. 11.** — The compound of hydrogen and fluorine is examined with so much difficulty that only one study is made of it.

In a small lead dish place about 5 g. of powdered fluor-spar. Next prepare a plate of glass, which is sufficiently large to cover the top of the lead dish, by covering one side of the glass with wax or paraffine. This is done by warming the glass over the lamp flame until it is hot enough to melt paraffine or wax. Place the paraffine on the hot glass, and, when it is melted, allow it to spread evenly over the surface of the glass. When cool, draw any figure or write whatever is desired on the paraffined glass, using a sharp, hard-pointed instrument for a pen, being careful to have the point reach the glass at every part of the lines.

Pour 10 cc. of sulphuric acid on the fluor-spar in the lead dish and immediately place the prepared glass on the dish, paraffine side down. Leave in this position for several hours. When the action is over, scrape off the paraffine and note the effect on the glass.

**Physical Properties.** — Hydrogen fluoride is a colorless volatile liquid, whose attraction for water is so great that it fumes in air. It boils at 19.4, and is converted into a solid at  $-102^{\circ}$ . The vapor density of the compound is 10. Its water solution, when distilled, yields a distillate containing about 37 per cent of the acid. When the liquid is dissolved in water the volume of the product is less than the sum of the volumes of water and acid. Its water solution has a specific gravity of 1.25, while the anhydrous acid has a specific gravity of .9879.

**Chemical Properties.** — Hydrogen fluoride is a very active substance, chemically speaking. It attacks most of the metals, producing compounds of fluorine and the metals, and sets hydrogen free. Gold, silver, and platinum are not acted upon by this compound. Its most characteristic chemical property is shown by its action on glass in the presence of moisture.



It decomposes the glass, forming with its silicon a gaseous compound. The compound is used to etch glass; the method of doing this etching is, in general, illustrated by Experimental Study, No. 11.

**Quantitative Composition of the Compounds of Hydrogen with each Chlorine, Bromine, Iodine, and Fluorine.** — The qualitative composition of these compounds has already been shown; that is, it has been shown that the first consists of hydrogen and chlorine, and nothing else; that the second is composed of hydrogen and bromine; the third, of hydrogen and iodine; and the fourth, of fluorine and hydrogen, and no other elements. The next question is, What is the quantity of each of these elements in definite amounts of these substances by mass and by volume? These determinations require the use of the balance and carefully prepared measures of volume. The processes used are those of analysis and synthesis.

**Analysis and Synthesis defined.** — By chemical analysis is meant the separation of the compound either into its elements or into certain recognized groups of elements. Analysis is qualitative or quantitative. In qualitative analysis the constituents of a substance are determined, while in quantitative analysis the amount by mass or volume of each of these constituents is determined.

Synthesis is the opposite of analysis in that the elements are united to produce a compound. It is practically a quantitative process, since known quantities of matter enter into the action.

**Analytical Study. — Experimental Study, No. 12. — (A) Volumetric Composition.** — (a) Fill a 400 cc. bottle with dry hydrogen chloride. (Be sure that the bottle is *full* of the gas.) (The gas is dried by passing it through sulphuric acid.) The bottle is tightly closed with a solid rubber stopper. Next introduce several pieces of sodium amalgam, and replace the stopper as soon as possible, being careful not to admit air. Shake the amalgam around in the bottle and allow it to stand

about five minutes, or until it becomes cool. Now invert the bottle, holding the mouth under water in the trough; remove the stopper, being careful not to permit any gas to escape, nor any air to enter the bottle. Place the bottle on the shelf of the trough and allow it to stand until the temperature has become constant. Lower the bottle into the water until the water inside of the bottle is on a level with that on the outside. Why? Mark the level carefully, remove the bottle from the trough, and test the gas with the burning stick. What is it? Determine the amount of this gas by volume and weight. (The student should be provided with a measuring cylinder; *e.g.* 25 cc. graduated to ccs.) If the work has been carefully done, it will be found that the remaining gas is hydrogen and that it fills one-half the volume of the bottle. What has become of the chlorine? What is the chemical relation between sodium and chlorine as shown in the study of chlorine? How much chlorine must there have been; *i.e.* by volume?

A more accurate result can be had by using a U-tube, like Fig. 3, having one arm graduated and furnished with a glass stop-cock. The gas is passed through the tube rapidly until it has displaced all the air. The stop-cock is now closed, the generating apparatus disconnected, and mercury poured into the open arm until it rises to the same level in both arms. Open the stop-cock until the pressure is equalized. Now close the stop-cock, and pass into the closed arm sodium amalgam, shaking until all the gas is

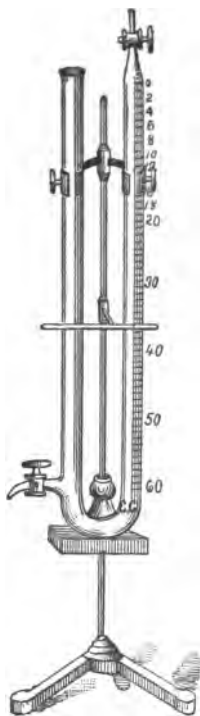


FIG. 3.

decomposed. The graduated arm enables the experimenter to determine the volume of gas remaining. This gas can be shown to be hydrogen by filling the open arm with mercury, thus placing the gas under pressure, opening the stop-cock, and igniting it.

(b) Again, by means of Hoffmann's apparatus (Fig. 4), or a similar form, decompose the gas and examine the products. The apparatus is filled with a concentrated solution of hydro-

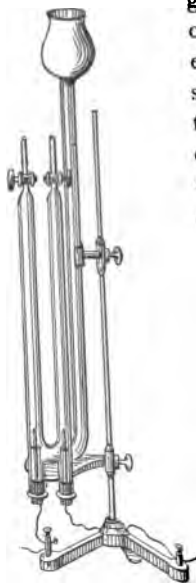


FIG. 4.

gen chloride which has been saturated with common salt. This last precaution is necessary to prevent the chlorine gas being dissolved in the liquid, it being not soluble in the mixture. The current from five or six cells of a Bunsen battery is passed through the solution. In a short time the gas will collect in each of the tubes over the poles of the battery. The gas at the negative pole can be shown to be hydrogen, and that at the positive pole can be shown to be chlorine. The volumes of the two gases are equal.

**Synthetical Study.** — Pass into the tube shown in Fig. 5 a measured volume of each pure hydrogen and pure chlorine, keeping the tube covered from the light. The tube must be completely filled with the mixture. (The gas may be prepared by decomposing pure hydrogen chloride when in its water solution.) Expose this tube to bright sunlight, or burn magnesium wire near the bulb. The gas changes color and a slight explosion occurs. If equal volumes of each gas have been used, the product is entirely colorless. (If unequal volumes are used, the hydrogen should always be the larger volume.) The tube is allowed to come to the atmospheric temperature, and one end is placed under

mercury and the stop-cock opened. The volume of the product is found to be the sum of the equal volumes of the hydrogen and chlorine. If water is placed on the top of the mercury, and the tube be raised out of the mercury so that the open end comes into the water, the gas is absorbed and the water enters the tube. The tube is completely filled, or not, according to the ratio of the volume of the two gases used. If any gas remains in the tube, it should be examined to determine what it is and how much it is by volume. It will be found that only hydrogen is present, and that the original volume of hydrogen less this volume is equal to the volume of chlorine used. The water solution of the gas in the tube should be removed and examined to prove that it is hydrogen chloride. How can this be shown?

Several other methods can be used to determine the volumetric composition of hydrogen chloride; *e.g.* the chlorine may be absorbed by a solution of potassium iodide. But whatever methods are employed, but one result will follow; namely, it will be proved that the compound consists of hydrogen and chlorine in equal volumes, and that when the gas is combined, whatever the volumes of the two gases that are mixed, equal volumes of each will unite to form this compound.

(B) **Gravimetric Composition.** — The gravimetric composition of this compound does not require any new chemical facts, but merely requires the application of mathematics and certain known physical facts.

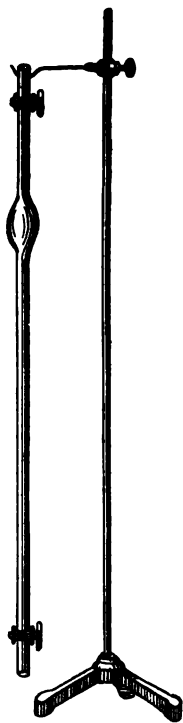


FIG. 5.

Let it be supposed that the tube used in the study just made has a capacity of 100 cc. Then if the tube be filled with the compound and it be decomposed, the tube will be filled with gas as before, but 50 cc. will be hydrogen and 50 cc. will be chlorine, according to the facts just established. For convenience, let it be supposed that the experiment is made at  $0^{\circ}$  temperature and under pressure of 760 mm. (It is supposed, however, that the student is familiar with the laws of Boyle and Charles and their application to the volume of gases. It would be well, therefore, to make the calculation under the actual conditions of temperature and pressure that obtain when the experiment is made.) Under the conditions named, the 50 cc. of hydrogen will weigh  $50 \times .0000896$  g., or .00448 g.; the 50 cc. of chlorine gas will weigh  $50 \times 35.37 \times .0000896$  g., or .1584576 g. Taking the weight of hydrogen as unity, these numbers stand in the ratio of 1 to 35.37. Therefore, since hydrogen unites with chlorine in but one proportion, one part, and only one, by mass, of hydrogen will unite with 35.37 parts of chlorine. Again, 1 vol. (*e.g.* 1 l.) of hydrogen will unite with 1 vol. or 1 l. of chlorine, the volume of the product being 2 vols. or 2 l. of hydrogen chloride gas.

**The Corresponding Study of the Compounds of Hydrogen with Bromine, Iodine, and Fluorine.** — A similar examination of these three gases shows similar facts to those discovered in reference to the composition of the compound of hydrogen with chlorine; namely, that they are composed of equal volumes of hydrogen and bromine, of hydrogen and iodine, and of hydrogen and fluorine, and that the volume of the compound is always the sum of the equal volumes of the constituent gases. By mass it is found that 1 part of hydrogen unites with 79.76 parts of bromine, with 126.54 parts of iodine, and with 19 parts of fluorine. It is also true that there is but one proportion in which they unite either by weight or by volume. (The student should apply these facts to the determination of the amount of

bromine or iodine in (say) a litre of each of the gaseous compounds, using similar facts; *i.e.* those of vapor density, decomposition of the compounds, etc.)

(a) **Meaning of the Term "Law," as used in Physical Science.**—The term *law* is quite general in its meaning as commonly used. It is common to speak of the law of custom, the law of the land, civil law, criminal law, scientific law, etc. In science it is necessary to use terms with definite and unchanging meanings. We ordinarily think of law as that which governs our actions. Consequently, it is sometimes defined as a rule by which certain matters are carried on, as, for example, the laws governing procedure in courts of justice. Scientific laws do not in any strict sense govern any action. Again, the origin and development of society laws are entirely different from those of scientific laws. Society laws are developed out of man's condition as a social being. They are formulated to meet the demands of society for self-protection, or as the result of certain conditions of society; for example, the laws forbidding trespass grew out of the necessity for the protection of property rights.

(b) **The Scientific Meaning of the Term "Law."**—Examine briefly the origin and development of a physical law, like Boyle's law in reference to the volume of gases under the influence of varying pressures. He examined the effect of pressure on the volume of gases, keeping the temperature constant. Starting with a given volume of air, he subjected it to increasing pressure, the amount of the increase being a constant quantity. An examination of these results discovered a common relation running through all his facts; *e.g.* if the pressure was doubled, he noticed that the volume was halved in each case. A study of other gases revealed the same set of facts. He formulated this into a statement, which is now given as follows: The temperature remaining the same, the volume of a given quantity of gas varies inversely as the pressure it

supports; or, the volume of a gas varies inversely as the pressure. This method of developing a physical law is illustrative of the process, in general, for the formation of scientific laws; *i.e.* for the laws of the physical sciences.

A law may therefore be defined as a statement in words of a common relation that characterizes a class of facts. It is readily seen that a law is not created to fit a new condition, or new conditions, but is merely a discovery by the human mind of what existed before, and an orderly and concise statement of the same.

It is true that the term *law* is applied to general truths, as in the case of Avogadro's law, which cannot be demonstrated by direct experiment; yet no experimental fact contradicts the fact or statement. It rests largely for its demonstration upon a conception of gaseous matter called the kinetic theory of gases. (This theory of gases should be understood by the student from its physical side before the study of chemistry is begun.) This theory has, however, an experimental basis. The term *law* is also sometimes applied to abstract truths, such as the law of motion.

**Law of Definite or Constant Proportion.** — In the study of the compounds of hydrogen with each of the elements chlorine, bromine, and iodine, it was found that for every 1 part by weight of hydrogen there were 35.37, 79.76, and 126.54 parts respectively of each of the elements mentioned. In no case has any other proportion been found. When these elements are mixed in varying proportions, and a chemical compound is formed by the proper means, 1 g. of hydrogen always unites with 35.37 g. of chlorine, and correspondingly for the other compounds. All the analyses and syntheses that have ever been made of these compounds have shown that these Proportions have never changed. Now a similar study has been made of nearly all chemical compounds, and the same general facts have been found; namely, that these compounds

have contained the same elements and in the same proportions by mass. This statement is called the law of definite or of constant proportions.

It may be stated again, as follows : In any chemical change the relative mass of the substances that enter into the change and the mass of the new substance are constant and unchanging.

**Law of Reciprocal Proportions.** — The experimental data for the illustration of this law have not been brought out thus far in our study, but it may be well to illustrate and state it in this connection.

It has been shown that hydrogen unites with chlorine in the ratio of 1 to 35.37 ; with bromine in the ratio of 1 to 79.76 ; and with iodine in the ratio of 1 to 126.54. 35.37 parts of chlorine combine with 23 parts of the element sodium, but 79.76 parts of bromine and 126.54 parts of iodine each combine with 23 parts of sodium. Also, 35.37 parts of chlorine combine with 126.54 parts of iodine. Facts of similar meaning can be shown in reference to other elements and other compounds. The law derived from these facts is stated thus : When each of two elements combine with another element, the proportion by mass of each represents the proportion in which they unite with each other.

**Historical Statements in Reference to the Law of Constant Proportion.** — **The Law of Multiple Proportions.** — The discovery of these laws is due to John Dalton, who published them in 1808 in a work called "A New System of Chemical Philosophy." He had, however, been experimenting for several years, beginning the study not far from the year 1800. He studied quite a large number of compounds and soon found that the law of constant proportions did not cover all the facts of mass proportions in the forming of chemical compounds. He found that certain combinations of the same elements did not contain the same proportion of the elements ; in other words, more than one compound of the elements was found to



exist. This discovery did not disturb the law of constant proportions, since this law had to do with the same compounds. A further study of chemical compounds showed that if the quantity of one of the elements *A* be considered fixed, and the lowest quantity of the other element *B* be considered as unity, the greater quantity or quantities of *B* were simple multiples of the unit quantity. He analyzed quantitatively, for example, two compounds of hydrogen with carbon. In one he found 14.3 per cent of hydrogen and 85.7 per cent of carbon, and in the other 75 per cent of carbon and 25 per cent of hydrogen. Now making hydrogen unity, it is readily seen that the proportions of the elements are 1 : 6 in the first case and 1 : 3 in the second case. Similar facts were found in reference to other compounds that he examined. This common relation or law is stated thus: When two elements combine in different proportions, if the mass of one of them is taken as unity, the masses of the other element entering into the compounds are simple multiples of the smallest mass of this latter element.

**Scientific Hypothesis and Theory.**—The word *hypothesis* literally means something “placed under”; *i.e.* a foundation or a starting-place. This is quite its meaning as practically applied. When the mind discovers laws among phenomena, it asks, What produces these phenomena? or what is the cause lying back of these laws? or what produces these common relations among the phenomena or facts? There must be some fact or cause which determines these facts. Thus, if the cause is not evident, a cause is supposed, and its adequacy is afterwards studied. It may be found to be right in many respects, but wholly inadequate in other ways; consequently, additions to and subtractions from the original supposed cause are made from time to time until eventually the supposed cause may be found to be a wholly sufficient cause. This study often leads to the discovery of many other laws and other causes that are practically quite distinct from the original

cause. It is in this manner that the physical sciences have been developed. Thus some laws are deductions and are not immediately dependent on experiment.

Starting with an hypothesis, the next step in advance is to a theory, and then finally the hypothesis or theory becomes a sufficient cause. The latter step, in many cases, is probably impossible, and the theory will always remain such.

**The Atomic Hypothesis.** — Dalton sought a cause for the laws of constant and of multiple proportions ; that is, Why do the elements combine as they do? What do these constant weights mean? He sought the answer in the constitution of matter. There are two possible conceptions of the constitutions of matter : —

*First*, That matter is perfectly continuous, or that it perfectly fills the space which it apparently occupies ;

*Second*, That it is made up of separate pieces or particles.

The first conception does not agree with the facts that we know to be true. If we think of a compound that we know consists of two kinds of matter, like that of hydrogen and chlorine, and we begin a division of it, it is evident that finally we must come to a piece of matter that if we divide further, one part is hydrogen and one part is chlorine. We know that physical division would not accomplish this result, but by chemical means it can be done, as was shown in the experiment with hydrogen chloride and sodium. Now this hydrogen piece of matter has never been divided further by any means. This indivisible piece of matter is called the atom. The name was used by early writers on the constitution of matter, and literally means indivisible. Dalton, however, gave the conception a new meaning and found in it an explanation of the laws that he had discovered. According to his view, matter consists of very small particles or atoms that cannot be divided either by physical or by chemical means ; that all chemical action is a combination of or changes in the combinations of

the atoms ; that atoms of the same kind have a definite and fixed mass ; that atoms of different kinds have different masses. Therefore, if compounds are decomposed or are composed, the ratio of the amounts of the elements in the compound will be the same ratio as that of the atomic masses.

Again, the law of multiple proportions finds its explanation in the atomic constitution of matter. Let the lowest proportion by mass of any elementary substance be the atom, and simple multiple proportion means that there are two, three, etc., atoms of the element in the compound. It can readily be seen, if matter is atomic in composition, that, were the atoms of the same kind, not of the same size and mass and shape, — in fact, did they not possess the same general properties, then compounds of the same elements, like hydrogen and chlorine, would not always be alike.

An atom, therefore, is the smallest mass of matter that enters into chemical combinations, or that can be removed from any chemical combinations. This hypothesis or theory has served as a working basis from which a large proportion of chemical science has been developed. Not the mere facts of chemistry, but the real body and substance of it.

**Atomic Weights or Atomic Masses.** — The expression *atomic mass* has been and is yet used to indicate what is really the relative masses of atoms. Weight, as commonly understood, is a measure of the force of gravitation acting on matter at the surface of the earth. It will therefore vary according to the place where the force is determined. While the mass of an atom, therefore, can never vary, — that is, it is not dependent on place and time, — its weight does change, according to its position on the earth's surface. Of course it can be said that "weight" may be and is made to include the two meanings. It is, however, considered more exact to use the word *mass* where quantity of matter is indicated, and *weight* where the force of gravity at the earth's surface is meant. The

unit of mass is the gramme, while the unit of weight is the dyne.

The mass of these atoms has been spoken of, but unfortunately it is only the relative mass that has been determined; that is, the mass of the atoms when some other atom has been taken as unity. The mass of the unit has not been determined in terms of our usual standards of mass. A close analysis will show that this is not far different from the ordinary method of determining mass by the usual standard. When it is said that a piece of matter weighs or has a mass of 10 mg., the mass is expressed in units, milligrammes; but our practical knowledge of a milligramme mass is not very definite. For example, place the milligramme "weight" in the hand, and we get no sensation of mass, as we do when the kilogramme "weight" is placed there. The eye sees a bit of matter, but its bulk changes with the kind of matter for the same apparent mass; e.g. platinum and aluminum weights. The unit of mass in weighing atoms is the mass of an atom of hydrogen. The absolute mass of this atom has never been determined, and hence other atomic masses are not known absolutely as so many grammes or milligrammes.

**Molecules.** — By the atomic hypothesis it has been seen that all chemical action is a change among the atoms of matter, and that a compound is produced by the union of the atoms; e.g. by the union of the atoms of hydrogen and chlorine. Further, that in the division of compound matter a quantity is finally reached such that, if any further division is made, the compound ceases to exist, and is separated into its elements or atoms. This small particle of matter is called a molecule; literally, a little mass. The chemist, therefore, looks upon all matter as made up of little masses or molecules, the units of mass. Each of these molecules contains a certain number of atoms, but under the same conditions always the same number; consequently, molecules of the same kind must always have a

definite mass. These units are therefore physical units. A molecule may be defined as the smallest portion of matter that can exist in a free state, or as that smallest portion of mass that possesses all the properties of the whole mass, bulk being excepted.

**Molecular and Atomic Masses.**—In the four compounds studied several facts have been established :—

(*a*) Those relating to the amount of each element present, by weight and by volume, in a definite quantity of each of the compounds.

(*b*) The weight of certain volumes of each gas, and therefore the density of each gas.

Taking the ideas of molecules, as just stated, it appears that the relative amount of each element in the molecule of each gas is known, since what is true of the whole mass must be true of its units, the molecules, it being made up of these equal units. It is found, for example, that for every 1 part by mass of hydrogen there are 35.37 parts of chlorine, 79.76 parts of bromine, 126.54 parts of iodine, and 19 parts of fluorine. The molecules of these kinds of matter, therefore, must contain these elements in the proportions named. Whether there are one or more atoms of these elements in the compounds cannot be ascertained from these facts. The proportions would be preserved if any multiple of these numbers is used.

**Avogadro's Law.**—A physical study of gases has led to the discovery of the law that equal volumes of all gases and vapors under the same conditions of temperature and pressure contain the same number of molecules. This law was first stated by Avogadro, an Italian chemist, in 1811. The cause of this law is not completely determined, but it agrees with a large number of physical facts. Maxwell has shown, on the assumption that the kinetic theory of gases is correct, that the law can be demonstrated mathematically. Although this is not capable of physical or chemical experimental proof, the facts of chemistry

as well as those of physics support its truth and do not in any marked instance contradict it. It is, in fact, one of the fundamental bases on which much of chemical reasoning rests, and in this work the law will be considered as demonstrated.

Now let us notice what new light this law gives in relation to molecular and atomic masses. When the litre of hydrogen and the litre of the compound of hydrogen and chlorine are compared as to mass under standard conditions, or when both gases are under the same condition, it is found that, taking the hydrogen volume as unity, the compound weighs 18.18 times as much, or, since a litre of hydrogen weighs .0896 g., a litre of the compound weighs 1.6289 g. Applying the law of Avogadro to this case, it is seen at once that the molecule of the compound of hydrogen and chlorine weighs 18.18 times as much as the molecule of hydrogen. The next question is, Shall the molecule of hydrogen or shall the atom of hydrogen (the half-molecule) be the standard of mass? If the atom is selected, it introduces the difficulty of determining the number of atoms in the molecule of hydrogen. If two atoms are present, it is readily seen that the number 18.18 must be doubled in order to express the molecular mass of the compound in terms of the hydrogen atom. The best evidence goes to show that such is the case; that is, that there are two atoms in the hydrogen molecule. Whether this is the atom or not, it is the half-molecule, and our standard of mass is often spoken of as the half-molecule of hydrogen.

The reasoning as applied to these compounds is as follows: It has been shown that 1 l. of hydrogen combines with 1 l. of chlorine, with 1 l. of bromine, with 1 l. of iodine, and with 1 l. of fluorine, and that in each case 2 l. of the product are formed. Since there are the same number of molecules in the litre of each kind of gas, let it be assumed that it is 100, or that it is 100  $n$ ,  $n$  being a constant multiple. When the union has taken place among these different gases, 2 l. of each of the gaseous

products are formed. Since they are under the same conditions, they must contain 200 molecules, or 200  $n$  molecules of each of the compounds. Now each molecule of the compounds must contain at least one atom of hydrogen and one atom of chlorine, etc.; therefore 200 molecules must contain at least 200 atoms of hydrogen and 200 atoms of chlorine, etc. But these 200 atoms come from 100 molecules, and therefore there must be at least two atoms to the molecule in the case of each of these gases. No facts contradict this conclusion and no facts show that there are more than two atoms to the molecule in the case of the gaseous elements under consideration, consequently the molecule of hydrogen is considered to have two atoms.

The molecular mass of this compound of hydrogen and chlorine is 36.36. Quantitative analysis shows that 97.3 per cent of this is chlorine and 2.7 per cent is hydrogen. Determining these per cents of 36.36 for each element, 35.37 parts is chlorine and one part is hydrogen. No compound has been found to contain less than this amount of chlorine; therefore this represents an atom of chlorine, and the compound contains one atom of hydrogen and one atom of chlorine. This number (35.37) is called the atomic mass or weight. It is also sometimes called the combining weight of chlorine, since this unit mass of chlorine is in all the compounds containing the element, according to this idea of an atom.

An atom of any element is sometimes defined as the smallest amount of that substance found in or separated from any compound.

If the same reasoning is applied to the other compounds of hydrogen with bromine and with iodine and with fluorine,—that is, taking into account the facts of volumetric and gravimetric analysis, of density, and that the amount of these elements found in these compounds is the smallest amount of each found in any compound,—it will be found that they consist of

one atom of each element combined with one atom of hydrogen, and that the numbers referring to these elements express their atomic masses. These numbers also express the only proportions in which these elements combine with hydrogen.

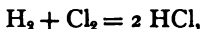
**The Symbols and Formulæ.** — The term *symbol* as applied to elements has been already sufficiently explained. It remains to symbolize the compounds. By the atomic hypothesis a compound is a union of elements, atom to atom, or atoms to atoms; it is therefore only necessary to write the symbols of the elements one after the other to represent the compound. This representation is called a formula. If more than one atom of the same kind exists in the compound, the number of atoms is indicated by writing the proper figures below and to the right of the symbol. For example, the compound of hydrogen with nitrogen contains three atoms of hydrogen and one atom of nitrogen, and is written  $\text{NH}_3$ .

The formula for the molecule of the compound of hydrogen and chlorine is therefore  $\text{HCl}$ , and is called hydrogen chloride. It means that one atom of hydrogen has united with one atom of chlorine; that one part by mass of hydrogen has united with 35.37 parts by mass of chlorine. When the gaseous molecule is represented, it also shows the amount by volume of the constituents in the molecule, and stands for a unit volume. The formulæ for the other compounds that have been studied are, accordingly,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HF}$ . They are called hydrogen bromide, hydrogen iodide, and hydrogen fluoride, in the order named.

A number written before a formula indicates that number of molecules; that is, it multiplies the whole molecule. For example,  $2 \text{HCl}$  means two molecules, or 72.74 units of mass. Where a molecule is enclosed in parentheses, with a number at the right and a little below, all of the molecules so included are multiplied; in other words, the parenthesis is used here as it is used in algebra.



**The Elementary Molecules of Fluorine, Chlorine, Bromine, and Iodine.** — The densities of these gases are 19, 35.37, 79.76, 126.54, in the order named. Hence their molecular masses are 38, 70.74, 159.52, and 253.08, respectively. Therefore there are two atoms to the molecule, and the volume molecules should be represented by  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ . The union of chlorine and hydrogen may be represented thus : —



and is read, one volume of chlorine plus one volume of hydrogen equals two volumes of hydrogen chloride ; or, two units of hydrogen plus 70.71 units of chlorine equals two times 36.37 units of hydrogen chloride, or 72.74 units.

---

## OXYGEN.

**Occurrence and Distribution in Nature.** — Of all the elements oxygen occurs in nature in the largest quantity and is the most widely distributed. It forms nearly one-half (about 48 per cent) of the earth's crust and eight-ninths of its water. It exists free in the atmosphere. It forms a large part (perhaps three-fourths) of all animal compounds and four-fifths of all plants.

**Methods of Preparation.** — (a) From the air.

(b) From water, by electrolysis.

(c) From various compounds, principally from potassium chlorate.

Oxygen is prepared by both physical and chemical methods. Since it is free in the atmosphere, this will seem to be its most natural source. It is, however, mixed with another gas, nitrogen, and it is with considerable difficulty separated. It has recently been separated by passing air over dull red-hot barium

oxide ( $\text{BaO}$ ), when another atom of oxygen is taken up and barium dioxide ( $\text{BaO}_2$ ) is produced. If now this compound is heated to a higher temperature, the oxygen taken up is set free and the barium dioxide becomes barium oxide. This same oxide can be heated again and more oxygen taken up, and at the higher temperature set free again. It should be noticed that heat and chemism are closely related; in fact, heat determines the chemical condition of the elements. If, for example, mercury is heated in the air to a temperature of about  $360^\circ$  for some time, it takes up oxygen, and a red compound is produced. If now this red compound is heated to a temperature above redness, the oxygen and mercury part company, the oxygen escaping as a gas, and the mercury collecting on the cooler parts of the containing vessel. Other compounds of oxygen with the metals behave in a similar manner when heated.

Oxygen is commonly prepared from a compound called potassium chlorate, which is represented by the formula  $\text{KClO}_3$ . When this is heated to a temperature of  $375^\circ$ , it yields its oxygen. When, however, manganese dioxide ( $\text{MnO}_2$ ) is present, the chlorate gives up its oxygen at a temperature not far from  $200^\circ$ . The explanation of this action is not satisfactorily made. It is probable that at a lower temperature than that at which the chlorate gives up its oxygen, when heated alone, the manganese dioxide takes oxygen from the chlorate, but that at a higher temperature it is given up again.

**Preparation.** — Intimately mix in a mortar 10 g. of potassium chlorate ( $\text{KClO}_3$ ) with 5 to 10 g. of manganese dioxide ( $\text{MnO}_2$ ). The material should be well dried and the dioxide should be free from organic matter and free carbon. (A little may be heated in an open tube to determine whether organic matter is present.) Place the mixture in a hard glass tube about 20 cm. long. (A common test-tube will answer if carefully heated.) Make the usual connections for collecting gases.

over water. Heat carefully until the gas begins to escape freely, and then remove from the flame, only heating sufficiently to keep up the flow of gas. Collect a sufficient number of bottles of gas, rejecting the first bottle collected. Remove the bottles from the trough as wanted, keeping them mouth upward and covered.

**Experimental Study, No. 13.** — (a) Examine for physical properties, according to the list of properties previously given.

(b) Test a bottle of the gas with a burning stick. Plunge the stick into the gas. Compare the rate of burning within and without the bottle. When the action ceases, tightly cover the bottle, and set aside for further examination.

(c) Place a piece of phosphorus the size of two pin-heads in the deflagrating-spoon, and lower it into the gas at ordinary temperatures. Then ignite the phosphorus and place it in the same bottle. (Clean the spoon each time it is used.) What are the white fumes? Of what must they be composed? Cover and set the bottle aside as before.

(d) Treat a piece of charcoal and a small amount of sulphur, each separately, in the same manner, setting aside the bottles for examination as before. Same questions as are given in (c).

(e) Use a piece of magnesium wire or ribbon 5 to 10 cm. long in the same manner as in (c). Cover and save bottle for further examination.

(f) Place a piece of sodium not larger than half a pea in the deflagrating-spoon, and study the action of the gas upon it at ordinary and at higher temperatures. Be careful not to lose any of the products.

(g) Into a small glass bottle full of oxygen pour 15 cc. of potassium hydroxide solution, then add 2 to 3 g. of pyrogalllic acid. Stopper the bottle tightly and shake thoroughly. Without removing the stopper, place the bottle with its mouth under the water in the trough and open the bottle. What has be-

come of the oxygen? This is a test for oxygen. What is a test?

(*h*) Another experiment showing the chemical relation of iron to oxygen may be shown as follows: Take a very fine iron wire and coil it into a spiral (by winding it around a lead-pencil); cover one end with sulphur by heating it and plunging it into the powdered sulphur. Then ignite the sulphur and place the spiral in a large jar of pure oxygen. The bottom of the jar should be covered with sand to prevent the breaking of the jar by the hot metal.

(*i*) Prepare a mixture of hydrogen and oxygen by generating the gases and passing them into a rubber gas-bag. Blow soap bubbles with this mixture, and while they are floating in the atmosphere, touch them with a burning stick. (It is not advisable for the student to perform this experiment unless it is done directly under the charge of the instructor.)

(*j*) Place two or three crystals of the potassium chlorate in a test-tube and heat until all the oxygen has escaped. Allow the tube to cool and dissolve the residue in water. Test the solution with a solution of silver nitrate, first adding a little nitric acid. What does this show? Compare with the test for hydrogen chloride. Dissolve a crystal of chlorate in 5 cc. of water and test it in the same way that the other solution was tested, only add but a single drop of nitric acid.

**Physical Properties.** — This study of oxygen shows that it is a gas, colorless, odorless, and tasteless; that it is only slightly soluble in water: 100 vols. dissolve only 4.1 vols. at  $0^{\circ}$ . It can be converted into a liquid at a temperature of  $-140^{\circ}$  and at a pressure of 325 atmospheres. Its density is 15.96.

**Chemical Properties.** — Oxygen does not readily unite with many elements at ordinary temperatures, but at high temperature the union is rapid and is accompanied with much heat and light. What is true of the elements examined in the previous study is true of most other elements, the action occurring,

however, with varying degrees of intensity. With hydrogen it unites with rapidity, producing explosive effects. If the gases are mixed, as in the oxy-hydrogen blow-pipe, or calcium-light jet, and ignited, the gases unite, forming a colorless flame whose temperature is among the highest produced. Oxygen and hydrogen do not unite until a temperature of about  $500^{\circ}$  is produced in the mixture. However, when the chemical change begins, the union produces a large amount of heat and continues until complete. One g. of hydrogen unites with 8 g. of oxygen, forming heat sufficient to produce 34,462 calories of heat.

Potassium pyrogallate in solution absorbs oxygen, the solution changing to a dark brown color.

**Examination of the Bottles from the Experiments with Oxygen.** — What has become of the substances in each bottle? What is the evidence of chemical change? Examine the contents physically; that is, examine odor, taste, and whether the product is a solid, a liquid, or a gas. Place a little water (20 cc.) in each bottle; shake, and touch the water with blue and red litmus paper.

We can easily infer that the substances placed in the jar have disappeared as such, and that in case of the carbon, phosphorus, and sulphur, the products in connection with water will change the blue litmus paper to a red color — that is, the water solution is acid; that in case of magnesium and sodium, under the same conditions, the product will not affect blue litmus paper, but will change the red litmus paper to the blue. In case of the iron no effect is produced on either kind of litmus paper.

Again, since only two elements were present, the compound in each bottle must consist of two elements; *e.g.* sulphur and oxygen, sodium and oxygen, etc.

**Tests for Free Oxygen.** — Oxygen is such an intensely active element that it is easily recognized. It may be distinguished

from nearly all other gases by its action on carbon; *e.g.* the rekindling of an ignited coal. It is also recognized by its action on the solution of potassium pyrogallate, as given under (*f*). Of course all air must be excluded from this kind of test.

**Name; Derivation; Meaning and Symbol.** — The name of this element is derived from two Greek words, *oxus* and *gennao*; the first meaning sharp or acid, and the second, I generate or form. The name was given to the element by Lavoisier because he supposed that all acid substances contained it. It has been shown already that the compounds of hydrogen with the halogens are acid. It will also be shown that many elements possess certain acid properties when united with a large proportion of oxygen, although they do not have these properties when the amount of oxygen is relatively smaller. For example, the metal chromium combined with one atom of oxygen (as  $\text{CrO}$ ) has no acid properties, but when combined with three times as much oxygen, as in chromic oxide ( $\text{CrO}_3$ ), it acts as an acid.

**History.** — Oxygen was discovered by Priestly in 1774 and by Scheele in 1775. It was first proved that the air contained two gases, and that one of these gases was the same as that produced when the oxide of mercury was heated above redness. It was left for Lavoisier to show the connection of this gas to ordinary burning, and to give it the name it now bears. It has been called empyreal air, vital air, and dephlogisticated air.

**Uses of Oxygen.** — Oxygen is necessary to respiration, or, in other words, to animal life. It is necessary to all ordinary burning, to decay, and to germination. It is used with hydrogen to produce the oxy-hydrogen light, or the Drummond light, employed in light-houses, and to fuse substances that require high temperature.

*The Compound of Oxygen and Hydrogen.*

## WATER.

**Distribution and Occurrence.** — Water is one of the most widely distributed compounds in nature. It not only occurs in large masses, as in oceans, rivers, etc., but it permeates the earth's crust everywhere. It forms a large per cent (about 75) of animal and vegetable substances. Vegetables like potatoes are largely water; *e.g.* potatoes contain 75 per cent, turnips 85 to 90 per cent, of water. Nearly three-fourths of the human body is water. It forms a large per cent of many solid chemical compounds, occurring as water of crystallization.

**Preparation.** — Since water is so abundant in nature it is not prepared chemically unless it is for experimental purposes. It can be prepared by the direct union of its elements, as has already been seen. It is formed as one of the products in many chemical actions.

**A Study of the Physical and Chemical Properties of Water.** — **Experimental Study, No. 14.** — (*a*) Fill a 500 cc. flask with water at (say) 15°, and crowd in a rubber stopper, in which is a No. 1 glass tube 30 cm. long. A thermometer, the bulb of which reaches an inch or so below the stopper, should also be used. A string or rubber band is placed around the glass tube and so fixed that it marks the height of water in the tube, which should be nearly full of water. Now place the flask, first, in water heated to a temperature of 40 to 50° and leave it for a few seconds; observe the height of the mercury in the thermometer and mark the height of water in glass tube. Second, place the flask in a freezing mixture made of powdered ice (or snow) and salt, covering the flask to the neck at least. Watch the column of liquid and the thermometer and make note of the result. Leave until the water begins to solidify.

(b) Take a strong 500 cc. flask and fill it about one-half full of water, placing it in position for boiling. Suspend a thermometer so that the bulb nearly reaches the water. Heat to boiling and determine the temperature. Upon what does the boiling-point depend?

(c) Remove the thermometer, and when the water is about to boil take the flask from the lamp; close it tightly with a rubber stopper and invert it, supporting it in the ring of the retort-stand. Pour cold water on the flask and notice and explain what occurs.

**Physical Properties of Water.** — When a thin layer of water is examined by transmitted light, it appears colorless; but if this layer become thick, the water takes on a bluish green color. Pure water is tasteless and odorless. It exists in three forms; that is, as a solid, a liquid, and a vapor, as determined by its temperature and the pressure upon its surface. When in its liquid form it expands with an increase of temperature at any point above  $4^{\circ}$ . When cooled from a high temperature it contracts until the temperature reaches  $4^{\circ}$ , when it expands until it solidifies. 100 vols. of water at  $0^{\circ}$  equals 107 vols. of ice. Therefore ice floats on water and serves as a protection against loss of heat from the water below, it being a poor conductor of heat. Water boils — that is, is rapidly converted into vapor without further rise in temperature — at  $100^{\circ}$  under one atmosphere pressure: at reduced pressure it boils at lower temperature.

**Chemical Properties.** — The experimental study of the chemical properties of water is taken up under so many elements that its particular consideration is omitted here. It has been found to be a neutral substance; that chlorine decomposes it in the light, setting oxygen free. Heat also decomposes the mixture of chlorine and water vapor, as when the mixture is passed through heated tubes. When water vapor is passed over red-hot or white-hot iron, the iron takes the oxygen, and the hydro-



gen is set free. As will be seen, many other metals slowly decompose it, either at ordinary temperatures or at high temperatures.

**Dissociation.** — Heat alone will decompose water into its constituent gases. This is true of many substances, and the term *dissociation* is applied to the phenomena. In general, by the term is meant the separation of a more or less complex compound into its elements or into less complex molecules. Water begins to decompose at  $1000^{\circ}$  and is half-completed when the temperature reaches  $2500^{\circ}$ .

**Water as a Solvent.** — **Solution, what?** — It is difficult to give in the form of a definition what is meant by solution. In general, the body disappears as a distinct body, and becomes in some way incorporated with the water. The solution may be colorless or it may take the color of the substance held in solution; e.g. when chlorine gas is dissolved in water the solution has a greenish color; potassium permanganate, a solid, yields a purple solution.

Although the phenomena of solution are not wholly understood, many facts are known, which may be best studied as follows: —

**Experimental Study, No. 15.** — (a) Place one-half g. of cane sugar in 50 cc. of water. Notice the physical action of the water on the sugar; that is, examine for taste, color, etc. Now permit the water to evaporate, using a low heat. Examine the residue. Do you get the same substance? Is the change physical or chemical?

(b) Add a piece of sodium, size of half a pea, to 25 cc. of water held in an evaporating dish. Cover loosely while the action goes on. Examine in the same way as (a). Do you get the sodium as a residue? Is the change chemical or physical?

(c) Dissolve a crystal of copper sulphate ( $\text{CuSO}_4$ ) in water, shake well, and determine whether the substance is uniformly

distributed throughout the water. If possible, allow it to stand for a day or so. Add a few drops of the solution to a large amount of water, and shake. Describe what occurs. How can you decide the uniform distribution of the compound? Allow the solution to stand in an evaporating dish for a few days. First evaporate off a portion of the water by heat.

(*d*) Put a few crystals of copper sulphate in a large test-tube, and fill it two-thirds full of water. Let it stand for a day or so without disturbing it. Describe what occurs. Is there evidence of unequal distribution of the copper sulphate?

(*e*) Take four test-tubes, numbered 1, 2, 3, and 4, and add to each 10 cc. of distilled water. To No. 1 add 5 g. of copper sulphate. To No. 2 add 5 g. of bichromate of potash. To No. 3 add 5 g. of common salt. To No. 4 add 1 g. of lead sulphate. (These substances, or salts, should all be powdered as nearly alike as possible.) Shake the tubes thoroughly and allow them to stand for a few minutes. Note the relative solubility at the temperature of the laboratory. Now boil the contents of each tube for a short time. What has occurred in each case? Allow the tubes to cool; that is, to stand for an hour or so. Boil again the contents of tube No. 1, and add powdered copper sulphate in small portions at a time as long as it dissolves. Allow it to cool. What occurs? Explain.

What inferences can be drawn from these facts as to the solubility of different substances, and as to the effects of heat on solubility?

(*f*) Turn off the clear liquid from tube No. 3, add a little more salt and bring the contents of the tube to boiling temperature. (No. 3 should have some undissolved salt in it.) Does more dissolve at this temperature?

(*g*) Place in each of two test-tubes 10 cc. of water. To one add two or three drops of carbon disulphide, shake thoroughly; to the other add 5 cc. of alcohol, and shake. Add another 5 cc. of alcohol to the latter tube, and shake. What becomes

of each substance? (Recall here the examination of gases studied as to solubility, especially hydrogen chloride.)

The following are a few of the facts established, which are typical of many similar ones : —

1. As to the general characteristics of solution of solids and liquids, we may infer (*a*) That solution in water may produce a chemical change ; that is, the identity of the substance may disappear, as in case of the metal sodium, but that often the substance has not undergone chemical change, since it may be recovered by removing the water or by its separating out, in crystalline form, on the cooling of the solution. (*b*) That when the substance is once uniformly distributed throughout the solution it remains so permanently. (*c*) That the amount held in solution depends on the nature of the substance, and in general, that the higher the temperature, the more of the solid the water holds in solution. That, however, there are exceptions to this conclusion, as is seen in the case of common salt, lime water, etc. That in the case of gases the opposite is true ; that is, the higher the temperature, the less of any gas is held in solution. (*d*) It can be shown that the quantity of the gas dissolved in water is proportional to the pressure on the surface of the liquid, and that when the solution is heated the gas, or gases, escape. It is also true that heat does not wholly expel all gases from their solutions ; that after a certain amount has been distilled, or driven off, the remainder escapes with the water vapor, the water always retaining a definite per cent of the gas. Hydrogen chloride illustrates this fact. This shows that there is probably a molecular compound formed between the water and, at least, a portion of the gas.

2. It may also be noticed that up to a certain point solution is continuous ; that is, larger and larger amounts of a given substance can be dissolved, while in a chemical change only one definite quantity of each substance enters into the change.

**Natural Waters.** — It has been seen that water dissolves solids, liquids, and gases; in fact, water is the most general solvent known. Therefore, natural waters will contain more or less of impurities, since water coming in contact with air will take up its gases, and from the earth's crust it will receive solid and liquid matter. The gases are taken up according to the law of Dalton. For this reason, the gas absorbed by water from the air is richer in oxygen than is the air itself. Oxygen is thus supplied to animals living in the water. The "air" absorbed by water contains about 15 per cent more oxygen than does the ordinary air.

Natural waters are constantly undergoing a cycle of changes in composition and in movements. From the soil, from bodies of fresh water, and principally from the ocean, it rises in the form of pure water vapor, due to evaporation. It is subsequently formed into the clouds, from which it is again precipitated as rain or snow, and is thus distributed over large areas. It gathers from the atmosphere whatever gases are there that are soluble. At the earth's surface it comes in contact with animal and vegetable matter which is undergoing decomposition, and it takes up soluble portions of this before sinking into the earth's crust. What it takes up from the earth's crust will depend, of course, on the kind of soil and rock over and through which it passes. If the rock is wholly insoluble, the water will be found to be nearly pure. Well waters, therefore, may contain a large or small amount of solid matter. Most of the solid matters that are thus dissolved are harmless in small quantities. (These substances will be spoken of under their proper heads.)

**Drinking Water.** — In general, it is the animal and vegetable substances that render water unfit for drinking purposes. A great excess of other solids, however, renders water unfit for such purposes. It is not generally the animal and vegetable substances themselves directly that are injurious, but the fact

that they undergo decomposition, owing to the presence of certain living organisms that produce compounds which are harmful. Also, these forms of matter serve for food for organisms that are harmful in themselves when taken into the human system. Thus water may contain disease-germs that cause typhoid fever, and when taken into the alimentary canal act directly or indirectly as the cause of the fever.

**Purification of Natural Waters.** — Natural waters are freed from sediment and mechanical mixtures, in general, by filtering; that is, causing the water to pass through sand, charcoal, and other insoluble substances, thus retaining these sediments. Since the gaseous and liquid impurities of natural water are few in number and small in quantity, it is freed from these impurities by distillation. This consists in converting the water into vapor and passing this vapor into pipes kept at temperatures considerably below  $100^{\circ}$ , thus condensing it to the liquid form. These pipes may be made of glass, tin, or any substance on which the water does not act.

### *Quantitative Composition of Water.*

**Volumetric Composition by Analysis and Synthesis.** — **Experimental Study, No. 16.** — There are various forms of apparatus for showing the volumetric composition of water. The essentials are, however, a current of electricity equal to that produced by from three to five Daniell cells, and an arrangement so that each of the poles of the current can be covered by a tube in order to collect the gases separately. Figure 6 presents a good form.

**Operation.** — The apparatus is filled with water acidified with sulphuric acid (10 cc. of water for 1 cc. of acid), and the connection made with the battery at the binding-screws. Notice the gas collected in each tube. Notice the amount at each

pole. What are these gases? The oxygen is slightly more soluble in water than the hydrogen, and also a small portion of the oxygen is converted into ozone (see page 89), and consequently the volume of oxygen is slightly less than one-half as much as the volume of hydrogen. The sulphuric acid is necessary to render the solution a better conductor of electricity. It probably enters in some way into the reaction, but the amount of the acid present finally remains unchanged.

**Volumetric Composition by Synthesis.** —

An apparatus like the one shown (Fig. 7) may be used to determine the synthetical composition of water.

If a straight eudiometer is used, it must be closed by a thick rubber pad placed in the mercury trough. (A description of the apparatus is of little value to the student. He should see it, and, if possible, handle and use it.)

Fill the apparatus shown in Fig. 7 with mercury, and pass into the closed limb *a* a definite volume each of oxygen and hydrogen. The tube should be graduated in cubic centimetres. Let 10 cc. of oxygen and 25 cc. of hydrogen be the volume of the gases passed into the tube. Of course the mercury must be drawn at the pinch-cock *c* until it stands at the same height in each limb. Cover the end of the tube with the thumb. A spark is now passed by means of a small Rhumkorrff coil placed in the circuit. Notice the volume of the



FIG. 6.

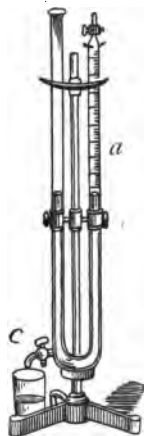


FIG. 7.

remaining gas and prove what this gas is. This experiment may be repeated several times, varying the quantity of each gas. Of course the water formed will be in a liquid state, and its volume will be very small. (What is the relation by volume of water to steam?)

In order to determine what the volume of the gaseous products is, it is necessary to surround the closed limb of the apparatus with a jacket through which the vapor of some body like amyl alcohol is passed. The alcohol exists as a vapor at temperatures above  $132^{\circ}$ . The gases are passed into the closed limb as before and the alcohol vapor passed through the jacket until the temperature becomes alike throughout the apparatus; that is, about  $132^{\circ}$ . The electric spark is passed as before, the two gases unite; but, the temperature being above  $100^{\circ}$ , the products remain in the gaseous condition.

From these experiments the following facts can be deduced:—

1. That when water is decomposed by the electric current, two gases are the products, the one collecting at the negative pole of the battery having twice the volume of the one collected at the positive pole; that these gases are hydrogen and oxygen, and are therefore elements.

2. That when oxygen and hydrogen are made to unite, two, and only two, volumes of hydrogen unite with one, and only one, volume of oxygen.

3. That the volume of the product is two-thirds the volume of the mixed gases; that is, three volumes of the mixed gases become two volumes of gaseous water.

**Quantitative Composition of Water by Mass.**—Several methods may be used to determine the quantitative composition of water.

(a) By calculation from volumetric facts. We have seen that two volumes of hydrogen unite with one volume of oxygen to form two volumes of gaseous water. It makes no difference

what the temperature is, provided both gases are at the same temperature and under the same pressure. Accordingly, the mass may be calculated at  $0^{\circ}$  and under one atmosphere of pressure.

For example, let us take 1 l. of hydrogen; then we know that  $\frac{1}{2}$  l. of oxygen will unite with it, and that the product will be 1 l. of gaseous water. Now, 1 l. of hydrogen weighs .0896 g. under the conditions just given. The mass of  $\frac{1}{2}$  l. of oxygen is  $\frac{1}{2}$  of  $15.96 \times .0896$ , or .715 g. Therefore, .0896 g. of hydrogen unites with .715 g. of oxygen, or, taking the amount of hydrogen as unity, the proportion stands 1 to 7.98. When this is calculated as per cents, the result is 88.86 per cent of oxygen and 11.13 per cent of hydrogen.

(*b*) **By Direct Gravimetric Analysis.** — The determination of the amount of oxygen in water depends on the great affinity of hydrogen for oxygen, which is especially marked at high temperatures. It also avoids the difficulty of weighing a gaseous substance. A compound of the metal copper and oxygen, whose exact composition has been determined many times, is used as the source of the oxygen. Next, pure hydrogen gas is manufactured and brought in contact with this copper compound, when it is heated to red temperature as above. The hydrogen unites with the oxygen of the copper compound, producing, as we know, water. The water thus formed is weighed. The water is saved by the action it has upon certain substances like calcium chloride, sulphuric acid, etc., over which it is passed. It is thus absorbed, and the gain in mass of the absorbing vessels gives the mass of water found.

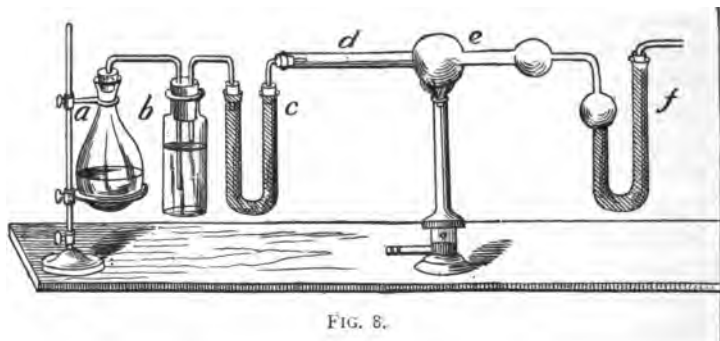
**Apparatus and Operation.** — The apparatus (Fig. 8) consists of a generating-flask *a* for preparing hydrogen, the wash-bottle *b*, containing either water or (better) a solution of potassium permanganate, and the U-tubes *c* and *f*, containing calcium chloride, which absorbs any water that may be in the gas. These pieces of apparatus are connected together and to the



tube *d*, which contains in the bulb *e* the copper oxide. The U-tube *f* is filled with calcium chloride and is connected with the tube *d*.

The exact amount of the copper compound is determined by accurate weighing, the tube *d* being weighed first, and again after the copper compound is placed in it. The mass of the tube *f* is also accurately known.

Hydrogen is now generated by the action of sulphuric acid on zinc, and made to pass through the apparatus until it is



completely filled with the gas. The tube *d* is then heated at the bulb to a red heat, and the gas continuously passed until the copper compound has been completely decomposed. How is this known? The apparatus is allowed to come to the temperature it had at the beginning of the experiment, and the tubes *f* and *d* are accurately weighed.

**Calculation of Results.** — This method of determining the quantitative composition of water was used by MM. Dumas and Boussingault as early as 1834, some of the determinations requiring from ten to twelve hours for their completion. For purposes of calculation the results of Dumas' experiment may be used.

Mass of <i>d</i> + copper compound	= 530.207 g.
Mass of <i>d</i> + copper compound after experiment	= 470.418 g.

Loss in mass, or amount of oxygen removed by hydrogen = 59.789 g.

Mass of tube <i>f</i> , that is + water (after the experiment)	= 493.640 g.
Mass of tube <i>f</i> before the experiment	= 426.358 g.

Gain in mass, or the amount of water produced = 67.282 g.

Therefore of this mass of water (67.282 g.), 59.789 g. is oxygen, or 88.86 per cent of whole amount. Now, since the remainder of the compound is hydrogen, 11.13 per cent of water is that element. Dumas made nineteen experiments, and found that 840.161 g. of oxygen produced 945.439 g. of water. Thus the average of all the experiments gives as the percentage composition of water : —

Oxygen	.	.	.	.	.	.	88.864
Hydrogen	.	.	.	.	.	.	11.136
							<hr/> 100.000

This method determines the amount of hydrogen by difference ; that is, it assumes that the mass of hydrogen is the difference between the mass of water produced and the oxygen required to produce it. The amount of hydrogen has been carefully determined by other methods, and this per cent (11.136) has been corroborated many times.

**Determination of Molecular Formula for Water.** — The following are the facts now established in reference to the compound water : —

(*a*) The fact that it contains 88.864 per cent of oxygen and 11.136 per cent of hydrogen, or one part of hydrogen to 7.98 parts of oxygen by mass.

(*b*) That its density as a gas is 7.98.

(*c*) That it is composed of two volumes of hydrogen and one volume of oxygen.

(*d*) That three volumes (two of hydrogen and one of oxygen) become two volumes when chemically united.

(*e*) That this is the smallest amount of oxygen that has been found in any molecule.

From previous reasoning it is seen that the molecular weight of the gas is 17.96, and that this molecule consists of oxygen and hydrogen alone. Therefore 88.864 per cent of the molecule is oxygen and 11.136 per cent is hydrogen, or 15.96 parts by mass are oxygen and 2 parts are hydrogen. Then, according to the fact stated in (*e*), this amount of oxygen is an atom, and this number (15.96) is the atomic mass of oxygen. The two parts of hydrogen correspond to two atoms, and the molecule should be represented by the formula  $H_2O$ . Again, taking the facts of volumetric analysis, we may reach the following conclusions: Since there are the same number of molecules in equal volumes of all gases under the same conditions, there are twice as many molecules of hydrogen as of oxygen that enter into the chemical change when water is produced from its element. And since two volumes of gas result from the union, there are two-thirds as many molecules of water as of the united number of molecules of oxygen and hydrogen entering into the change. The two molecules of hydrogen contain four atoms, and therefore the two molecules of water formed contain two atoms each of hydrogen. Assuming, as demonstrated, that a molecule of each gas contains two atoms, four atoms of hydrogen and two atoms of oxygen form two molecules of water-gas, or there are two atoms of hydrogen and one atom of oxygen to the molecule of this gas, and its formula should be  $H_2O$ .

**The Number of Atoms in a Molecule of Oxygen.** — The density of oxygen gas is 15.96. Hence its molecular mass is 31.92; since its atomic mass is 15.96, there are two atoms to the molecule of oxygen.

The following is a statement of the composition of some of

the compounds containing oxygen, the substances being gases, or can be converted into gases : —

SUBSTANCE.	Vapor Density.	Molecular Mass.	Per Cent of Oxygen.	Amount of Oxygen.
Water . . . . .	8.98	17.96	88.86+	15.96
Nitrogen chloride . . .	32.67	65.34	24.42+	15.96
Carbon dioxide . . . .	21.95+	43.89	72.72	31.92
Carbon monoxide . . . .	13.96+	27.98	57.14+	15.96
Sulphurous anhydride . .	31.95	63.90	50.00	31.92
Sulphuric anhydride . . .	39.98	79.96	60.00+	47.98
Nitrous oxide . . . . .	21.98	43.96	36.31	15.96

An examination of these facts shows that the amount of oxygen in any of these molecules is never less than 15.96, and that all other amounts are multiples of this number. Other facts of similar character might be added, but all would show this one fact,—that 15.96 parts by mass is the smallest amount that is found in any of these gaseous molecules.

## OZONE.

**Occurrence.** — Ozone occurs in small quantities in the atmosphere, especially after electrical disturbances like a thunderstorm.

**Methods of Preparation.** — It is prepared (*a*) from pure oxygen by the action of what is called the silent electrical discharge.

(*b*) It is produced when the phosphorus slowly unites with oxygen. It is also formed when an electrical induction machine is worked.

**Preparation and Experimental Study, No. 17.** — (a) A stream of dry oxygen is passed through a Siemens tube, the escaping gas being passed into a tall beaker in which are suspended strips of paper moistened with a solution of starch and potassium iodide. Make the proper connection with either an induction machine or with a Rhumkorff coil. Pass the gas through a solution of potassium iodide. Prove that iodine is set free. Test the solution of potassium iodide with litmus, and then the solution through which the changed gas has been passed. Note the results for future study.

(b) Place in the tall beaker two pieces of freshly cut and scraped common phosphorus, each about 2 cm. long, and add sufficient water to cover all but about one-half cm. Cover the beaker and allow it to stand for an hour or more. Examine the gas by the nose and the strips of paper prepared as just given. What produced the change in the oxygen of the air? What is the result of bringing oxygen in contact with phosphorus? What effect does the water present have?

(c) Place a little mercury in a porcelain crucible (or use the deflagrating-spoon), and lower it into the gas in the beaker. Cover the beaker, leave for a few minutes exposed to the gas. Remove, and examine the mercury. How does ordinary air, or pure oxygen, act on the mercury?

(d) Pass the oxygen made by decomposing water by means of the electric current through ether. Test the gas before passing through the ether and after it has passed through it, by means of the starch and iodide paper. Use the ordinary apparatus for decomposing water, by attaching a rubber tube to the terminal of the tube collecting oxygen. The other tube may be left open. It is best to acidulate the water with chromic acid, but sulphuric acid may be used as before (1 of acid to 21 of water). Let the gas pass for some time, say one hour. Add a little of the ether solution to an indigo solution. Shake, and if the color is not destroyed, add more

of the solution. Has heat been used in any of the reactions studied? What is the agent?

**Physical Properties of Ozone.** — Ozone is a gas under ordinary conditions, possessing an odor suggesting that of chlorine; that is, when the latter is much diluted by air. The purer the gas, the more pungent and irritating the odor. When pure oxygen gas is subjected to the electric discharge, only a small amount of it is changed to ozone. It is, however, more easily liquefied than oxygen, and consequently when this mixture is passed through a tube the temperature of which is sufficiently low the ozone condenses to a steel-blue liquid and the oxygen is uncondensed. This temperature is about  $-180^{\circ}$ . This liquid boils at  $-160^{\circ}$ , the gas having a blue color. The density of the gas is 24. It is stable at very low temperatures, but at ordinary temperatures it is slowly converted into ordinary oxygen. The higher the temperature, the more rapidly does this action take place, and at  $200^{\circ}$  the change takes place explosively.

It has been shown that the volume of oxygen is reduced two-thirds when it is completely ozonized. Ozone is soluble in ether.

**Chemical Properties.** — Chemically speaking, ozone differs markedly from oxygen. It attacks many substances at ordinary temperatures that oxygen only attacks at high temperatures, and is thus tested for, or distinguished from, oxygen. It sets iodine free from iodides. (Chlorine sets iodine free, but the solution does not become alkaline.) It unites with silver and mercury, which ordinary oxygen does not attack at the usual temperatures. It almost instantly bleaches indigo solutions and rapidly destroys organic matter. Some have ascribed the bleaching of ordinary colored cotton goods, when they are spread on the ground or snow, to the ozone in the atmosphere.

**The Ozone Molecule.** — It has been shown that the molecule of ordinary oxygen contains at least two atoms. Under the

same conditions the molecule of ozone contains three atoms, since its density is 24, its molecular mass is 48, and the atom of oxygen has a mass of 16.

The same conclusion may be reached by considering the facts in reference to its volumetric relation to oxygen. Since under the same conditions gases contain the same number of molecules, the molecule may be considered as a unit-volume, and  $O_2$ ,  $H_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $F_2$ , represent equal volumes of each of the substances indicated. The volumetric changes in ozonizing oxygen may be represented thus:  $3 O_2 = 2 O_3$ . That is, three volumes of oxygen become two volumes of ozone.

**Nascent State.** — When ozone decomposes, one of the products is common oxygen, so that a single molecule  $O_3 = O_2 + O$ . Of course, when it decomposes spontaneously, two molecules  $2 O_3 = 3 O_2$ , the reverse of the changes in its formation. If, now, there is present some substance with an affinity for oxygen, this single atom unites with it instead of with another atom of oxygen. An element in this condition is said to be in a nascent state; that is, the condition at the instant of being set free from its combinations.

It has been stated that when hydrogen and oxygen unite, a certain definite quantity of heat is evolved; that is, 34,180 calories when 1 g. of hydrogen unites with 8 g. of oxygen. Now, before the molecule of water can be formed, the molecules of hydrogen and oxygen must be decomposed, and a definite quantity of heat is necessary to produce this decomposition. If, therefore, the atoms are already free, we should expect the chemical activity to be correspondingly increased, other conditions being the same.

**Allotropism.** — Several elements have the property of assuming different forms when subject to special conditions. This property is called *allotropism*. The word *allotropism* is derived from two Greek words, signifying another mode or form. Ozone is oxygen, and nothing else, so far as matter is con-

cerned ; but it presents new properties, and under a casual observation might be considered another substance. The only real difference between it and oxygen, outside of its physical and chemical properties, is that its molecule contains three atoms, on the same basis that the molecule of oxygen contains two atoms. Some of the other cases of allotropism are explained in the same manner ; *e.g.* see under SULPHUR.

**Name and History.** — The name *ozone* was given to it by Schönbein, because of the odor of this form of oxygen, the word meaning "I smell." In 1840, while decomposing water by an electric current, he noticed that the oxygen had an odor like that produced by an induction electrical machine. This led to the conclusion that there was some connection between this odor and oxygen. In the same year two other scientists showed that ozone was a modified form of oxygen. Later — namely, in the years 1852 to 1860 — the facts that oxygen can be wholly converted into ozone, and that this product has a density of 24, were proved.

**Uses.** — Ozone is used medicinally as generated by electrical machines. It is said to relieve asthma. As produced in nature it is thought to rapidly destroy decaying organic matter. It is also used for bleaching and as a disinfectant.

---

## SODIUM.

**Occurrence and Distribution in Nature.** — Sodium as an element does not occur free in nature, owing to its chemism for other elements. It occurs, however, in large quantities combined with chlorine in the compound known as common salt. It occurs in animal and vegetable substances, in soils, and in many rocks, such as feldspar, cryolite, Chili saltpetre, and in a large number of chemical substances. It is an interesting fact



that plants living in sea-water gather largely of sodium compounds and only a small amount of potassium compounds, while land plants reverse the process.

**Experimental Study, No. 18.** — Since this element is not easily separated from its compounds, a discussion of this subject will be taken up later, and the element will be here studied without reference to its preparation.

(a) The usual study of physical properties.

(b) Use a piece of sodium as large as a pea, and place it in 50 cc. of pure water in an ordinary evaporating-dish. Loosely cover the dish, and note and describe what takes place.

(c) Place a piece of the same size on a small block of ice, and note and describe what takes place. What physical property can be learned here? What becomes of the sodium? Evaporate the solutions (b) and (c) to dryness, being careful not to overheat. (This evaporation can be done in water-bath or by placing the evaporating-dish several inches above the flame of a Bunsen burner; at least, after most of the water has been driven off.) Examine the residue, by taste, touch, etc., by litmus paper, blue and red.

The action of sodium towards chlorine, bromine, and oxygen may be repeated; at least, they should be recalled and studied here.

(d) Use a piece of sodium the size of a large pea and a piece of copper gauze about 2 cm. square. Make a cylinder of the gauze by wrapping it around a lead pencil; bend one end of the cylinder up so as to close it. Now drop the sodium into the cylinder and close the other end firmly. (Be sure that the gauze and fingers are free from water.) Now grasp the cylinder firmly with the pincers and quickly plunge it under the mouth of a gas-bottle, prepared as it would be for the collecting of gas over water. Hold it here until all action ceases. Examine and recognize the gas that is thus made. Use the burning-stick test. From whence is this gas? Where is the sodium?

(c) Again, prepare a tube (glass) 2 cm. long of No. 1 tubing, closing one end. Carefully dry the tube and weigh it, and fill it with sodium by forcing the tube into a piece of sodium, where it is freshly cut, until it is full. Now remove this tube and crowd the sodium into it so that no air is left in the tube. It should be left nearly full. Next weigh as quickly as possible; but if any delay is necessary, it should be placed under gasoline or naphtha until used. Fill a graduated tube with water and invert it in the trough for collecting gas. Now quickly bring the tube containing the sodium under the mouth of the graduated tube and hold it until all action ceases. Allow the apparatus to stand until it has reached the temperature of the surrounding air. Equalize the pressure within and without the tube and read the volume of the gas.

**Calculation of the Amount of Hydrogen set Free.** — Suppose that the volume of gas is found to be 80 cc., under pressure of 760 mm. and a temperature of 20°. Subtracting the pressure of aqueous vapor, 17.4 mm. for this temperature, the pressure due to the hydrogen is found to be 742.6 mm. Now find the volume of the gas under standard conditions by the use of the following formula: —

$$V = \frac{v(P - a)}{760(1 + .00366 t)}$$

Under these conditions the volume of the gas is found to be 71.6 cc. This amount of hydrogen has a mass of .006415 g., since 1 cc. weighs .0000896 g. under these conditions.

The amount of sodium taken was .1474 g. Hence .006415 g. of hydrogen is set free from water by .1474 g. of sodium. Several determinations may be made.

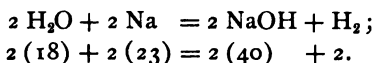
The formula for water has been determined to be  $H_2O$ . When the solid product of this action is examined, it is found to contain hydrogen, oxygen, and sodium. Recalling the conception that all chemical changes are changes in the mole-

cule, it will appear that the following represents this chemical change :  $\text{H}_2\text{O} + \text{sodium} = \text{H} + \text{a compound containing sodium, oxygen, and hydrogen.}$

Since there are but two atoms of hydrogen in the molecule of water, — and hydrogen is left in the molecule of the new compound, and hydrogen is also set free, — there must be one atom set free and one atom left in the compound. Also, when this compound is treated with more sodium, all the hydrogen is set free, and the quantity of it is just equal to the amount set free by the first reaction. Sodium, therefore, replaced one atom of hydrogen ; and taking the amount of hydrogen as a unit, it is found that the amount of sodium is equivalent to 22.98 such units. This, therefore, is the exchange mass or equivalent of sodium for one atom of hydrogen. This is taken as the atomic mass of sodium. The formula for the compound formed by the action of sodium on water is  $\text{NaOH}$ , and is called *sodium hydroxide*.

Let us weigh the water that is used in the reaction of sodium and water, the dry solid that is produced, and the hydrogen that is set free. The following are the facts of an actual experiment : One gramme of sodium was used. It set free .0435 g. of hydrogen. The solid substance that was left, after drying, weighed 1.74 g. The original weight of the water taken was 10 g. The amount of water that escaped by evaporation was 9.217 g. ; *e.g.* the water left undecomposed. Therefore there was .783 g. of water that entered into the reaction. .74 g. of the new compound must, therefore, have come from the water, and must be either oxygen or hydrogen, alone or both combined. The combining "weight" of sodium is 23. Therefore, if 23 g. or units of sodium had been used, 40 g., or  $23 \times 1.74$  g., of the new compound would be formed, or 17 g. or units besides the sodium. One of these units is hydrogen, and 16 are oxygen ; but 16 is the equivalent of oxygen when hydrogen is 1.

The chemical changes can be represented as follows : —



Or,  $18 : 23 :: x (.783) : 1,$

the amount of water in the example given ; or, —

$$1 : 40 :: .0435 : (1.74),$$

amount of sodium hydroxide.

**Physical Properties.** — Sodium is a solid at ordinary temperatures, having a silvery metallic lustre. It is soft, being easily cut with a knife. It is lighter than water, as was shown by its floating on water. Its vapor density has not been satisfactorily determined, although it is a gas at red heat. The best results in this determination shows the density to be about 23, and in this condition therefore has two atoms to the molecule.

**Chemical Properties.** — Sodium is a very active element, chemically speaking. It unites with many of the elements at ordinary temperatures ; *e.g.* chlorine, bromine, iodine, and oxygen. When placed in water it decomposes it, setting one-half of the hydrogen free. The new compound formed is a solid readily soluble in water, and changes red litmus paper to blue. It produces a taste called alkaline.

**Name and History.** — The symbol Na is derived from the word *natrium* (or *natron*), an ancient name for the natural deposit of sodium carbonate. *Sodium*, the common name, is derived from the word *soda-ash* (or possibly *sod-ash*), since one of its compounds was obtained from the ashes of burned sea-plants.

Sodium was first separated from its compounds by Sir Humphry Davy in the year 1807. Up to this time the compound sodium hydroxide (NaOH) was considered an element. Davy

subjected it to the action of a powerful electric current, when it was decomposed, the sodium gathering at the negative pole of the battery.

---

## POTASSIUM.

**Occurrence and Distribution in Nature.** — Potassium is widely distributed in nature, in both mineral and organic matter, and in compounds similar to those in which sodium is found. It resembles sodium in most of its properties, and is consequently never free in nature. The method for its preparation will be considered later on, under the study of metals.

**Experimental Study, No. 19.** — Potassium should be examined in the same manner that sodium was examined.

**Physical Properties.** — Potassium is a solid at ordinary temperatures, lighter than water. When freshly cut it presents a silver-white, metallic lustre. In general, it has the same physical properties as the metal sodium.

**Chemical Properties.** — Potassium is more active, chemically speaking, than sodium, uniting with the same elements with greater rapidity and with the production of a greater amount of heat and light. Its action with water is very rapid, one-half of the hydrogen of the water being set free and a compound of potassium, oxygen, and hydrogen, having the formula  $\text{KOH}$ , is formed. It is found that one part of hydrogen is set free by 39.03 parts of potassium. This compound has, in general, the same properties as does the corresponding sodium compound  $\text{NaOH}$ ; *i.e.* it is alkaline to the taste, and changes red litmus paper to blue, or it is an alkali. Its formula is  $\text{KOH}$ , and in chemical language is called potassium hydroxide. The reasoning and the facts by which this formula is determined are the same as those used in deciding what the formula should be for the corresponding compound of sodium.

**Name and History.** — The symbol K is derived from the word *kalium* (or *kali*), the Arabic word for ashes, from which the element may be prepared. The name *potassium* is derived from *pot-ash*, which is the name of the impure potassium carbonate obtained from wood ashes.

The element was discovered by Sir Humphry Davy in 1807. He decomposed potassium hydroxide by means of a powerful current of electricity.

**Relation of Acids and Bases.** — Of the compounds studied, when tested with litmus paper, all but one (water) have produced changes of color, either from blue to red or from red to blue. These compounds are, therefore, divided on this basis into two classes, to which the names acid and alkali (or bases) are given. The term *base* is more inclusive than the term *alkali*, but both are hydroxide compounds. (See further on.) These compounds, acids and alkalis, may be taken as typical of two great classes of substances that sustain definite chemical relations to each other.

**Experimental Study, No. 20.** — (A) An examination of their chemical relations to each other.

**Apparatus.** — Two burettes, 25 or 50 cc., or two 25 cc. graduated cylinders, and the necessary beakers. (Two pipettes may take the place of a burette.)

**Materials.** — A solution of hydrogen chloride of definite strength; that is, a solution so made that the exact quantity of the substance in each cubic centimetre is known; also similar solutions of each sodium and potassium hydroxide. Let it be supposed that the hydrochloric acid solution contains .03637 g. per cubic centimetre of the acid, and that the alkali, sodium hydroxide, contains .04 g. for every cubic centimetre of the solution; and that the potassium hydroxide solution contains .056 g. of the alkali for every cubic centimetre of solution. These solutions can be made sufficiently accurate by quickly weighing 4 g. and 5.6 g., respectively, of each substance and

putting each into (say) 90 cc. of water, dissolving, allowing to cool, and making up the 100 cc. How much of the alkali will each cubic centimetre contain? What part of the solution is made use of here?

**Operation.** — (a) Experiment with a litmus or on a phenolphthalein solution, to determine how much is required to produce the changes; that is, from acid to neutral or alkaline to neutral. (These substances are called indicators.) Suppose that one-hundredth of a drop of either the acid or the alkali solution is required to produce the change. How much alkali or acid is used, the solutions having the concentration just given?

(b) Run 5 cc. of the acid solution into a beaker, and add a few drops of the indicator. Now run in carefully from the other burette the sodium hydroxide solution, finally drop by drop, stirring constantly. Be careful not to add an excess. Note how much of the alkaline solution is needed to change the color of the indicator.

(c) Take 10 cc. of the acid solution and proceed as before, noting the amount of the alkaline solution used.

---

<sup>1</sup> Since most of these substances, as found in market, are impure, the instructor should determine beforehand how much is necessary to be weighed in order to get the amounts of the pure alkali thus indicated.

A solution containing a known per cent of hydrochloric acid should be given the student. He should prepare the standard acid solution, finding from a table how much acid there is in each cubic centimetre, from the density corresponding to this per cent of acid. He should then calculate the amount of acid solution to use in making the acid standard solution. For example, he is given a solution containing 32.22 per cent of hydrogen chloride and having a specific gravity of 1.16. In each cubic centimetre there is, therefore, of real acid .3222 times 1.16, or .373952 g. A 10 per cent solution of acid has a specific gravity of 1.02, and consequently contains .0102 g. of hydrogen chloride per cubic centimetre. Suppose now 100 cc. of such a solution is desired. Each cubic centimetre of the original solution contains .373952 g. of acid, and 100 cc. of the dilute solution contains 1.02 g. of acid. It will require therefore as many cubic centimetres of the original solution as .373952 is contained times in 1.02. This is 2.7 +; therefore 2.7 cc. of the acid is taken and diluted to 100 cc. Of course, this method only gives fairly accurate results.

(d) Take 15 cc. of the solution and proceed as before.

(e) Take 20 cc. of the solution and proceed as before.

Arrange the results in columns. Calculate the amount of each substance used in each case.

(f) Proceed in exactly the same way with the potassium hydroxide solution.

Tabulate the results and note the quantity of acid and alkali in each case. The following is a table of results : —

Acid Solution. HCl — .03637 g. per cc.	Sodium Hydroxide. NaOH — .04 g. per cc.	Potassium Hydroxide. KOH — .056 g. per cc.
10 cc. required.	10 cc.	10 cc.
15 cc. “	15 cc.	15 cc.
20 cc. “	20 cc.	20 cc.
25 cc. “	25 cc.	25 cc.
Or, .3637 g. “	.4 g.	.56 g.
.5455 g. “	.6 g.	.84 g.
.7274 g. “	.8 g.	1.12 g.
.91025 g. “	1.0 g.	1.40 g.

What relation exists between the sets of numbers? How much real acid and how much real alkali were used in the first case?

The mixture produced in each case is said to be neutral; that is, either colored litmus solution will not be changed.

(g) Weigh about 4 or 5 g. of sodium hydroxide, and dissolve in an evaporating-dish in 50 cc. of water. Add the indicator, and run in the acid solution until the neutral point is reached. Evaporate the solution to dryness. Compare the residue with the substances from which it is formed. Examine by taste. What does it taste like? It consists of chlorine and sodium. What is its formula?

(B) **Conclusions.** — (a) The first conclusion is that neutralization is a chemical action, since entirely new products are formed.

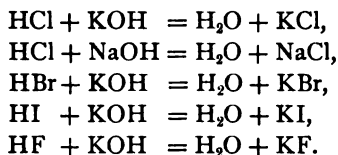


(*b*) That, like a chemical change, definite quantities of matter enter into the change. See table of results just given.

(*c*) The new compound is neither an acid nor a base.

(*d*) In (*g*) common salt is formed.

Now what is true of this acid and these bases is true of all the acids studied, — in fact, is true, in general, of all acids and all bases. It has been seen that the acids thus far considered contain hydrogen united with another element, and that the bases contain hydrogen, oxygen, and a metal. Now what takes place in the molecules during these changes? The molecules are HCl, HI, HBr, NaOH, and KOH. We have already seen one atom of hydrogen in water replaced by one atom of sodium. We have also seen the great affinity between sodium and potassium, and chlorine, iodine, and bromine. The sodium of the base and the hydrogen of the acid exchange places; and since one atom of sodium replaces one atom of hydrogen, the formula for the new compound is NaCl. The other compound formed is water. The same reaction, in general, is true of the other acids and the other base. The new compounds have these formulæ: KCl, KI, KBr, Na, Br, NaI. These changes may be written as follows: —



We may now say that a base is a compound of hydrogen, oxygen, and a metal, and that the metal may be replaced by the hydrogen of an acid, the metal uniting with the remainder of the acid. Further, the products are a neutral substance called a salt, and water.<sup>1</sup>

---

<sup>1</sup> There are exceptions when the product is not neutral; that is, either the acid or the alkaline (or basic) property may still exist. Such cases are considered when they are reached.

Many of the bases change red litmus solution to a blue color.

An acid, as thus far studied, is a compound of hydrogen and some one of the chlorine group. It changes blue litmus paper to a red color, and has an acid taste. Its hydrogen can be replaced by a metal, as for example by sodium.

**Nomenclature.** — The word *nomenclature* is derived from *nomen*, a name, and *calo*, to call, and therefore signifies calling, or giving names.

It may be conveniently studied under the following heads : —

1. Nomenclature of elements.

2. Nomenclature of molecules or compounds. (*a*) Binary molecules ; that is, molecules consisting of two kinds of atoms or groups of atoms.

(*b*) Ternary molecules ; that is, molecules consisting of three kinds of atoms or groups of atoms.

The nomenclature of elements has already been sufficiently explained in the introduction.

(*a*) The method of representing a compound or molecule has been already given. It remains to give the method of naming the compound. In general, binary molecules are named from the atoms that make them up. The possible differences in compounds containing the same elements is in the number of atoms of each element present in the molecule ; that is, the only difference that affects its name. The only classes of binary compounds or molecules to provide names for are, therefore, first, those compounds of which only one combination of the atoms composing it is known ; second, those compounds of which more than one combination of the atoms composing it is known.

The constant in this naming is that the most strongly negative element, usually a non-metallic element, is written last, and to its name the termination “ide” is applied, generally, in place of the last syllable ; and if but one compound is known, the name of the element written first is used unchanged in the com-

plete name of the compound. For example,  $\text{HCl}$  is hydrogen chloride (ine = ide) ;  $\text{KI}$ , is potassium iodide ;  $\text{H}_2\text{O}$ , hydrogen oxide ;  $\text{NaBr}$ , sodium bromide, etc.

If one element varies as to the number of its atoms in the molecule, the Greek numerals are prefixed to the name of the varying element, thus indicating the number of atoms of the element in the compound. The numerical prefixes are "mono," "di," "tri," "tetra," "penta," "hexa," "hepta," "octa," etc., the ordinary rules of euphony being observed in their use. For example, a compound containing five atoms of oxygen is not written penta-oxide, but pentoxide.  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_3$ ,  $\text{Cl}_2\text{O}_5$ , are called chlorine monoxide, chlorine trioxide, and chlorine pentoxide, respectively.

If both elements vary as to the number of atoms in the molecule, the numerals are applied to the names of both elements. Thus,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ , are plumbic oxide, plumbic dioxide, and triplumbic tetroxide, in the order named.

The same prefixes and suffixes are sometimes used to distinguish binary molecules that are used for ternary molecules ; namely, "ous," "ic," "hypo," and "per." They are applied to both elements in the manner explained under ternary molecules. Thus,  $\text{Hg}_2\text{O}$  and  $\text{HgO}$  are called mercurous and mercuric oxide, respectively.  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_3$ ,  $\text{Cl}_2\text{O}_5$ , are called hypochlorous oxide, chlorous oxide, and chloric oxide, in the order named. There are also some common names that are used for a few compounds such as hydrochloric acid instead of hydrogen chloride ; sesquioxide of iron instead of trioxide or ferric oxide.

(b) **Ternary Compounds.** — These molecules are divided into three classes for purposes of naming ; namely, acids, bases, and salts.

1. *The Naming of Acids.* — For the purpose of naming, an acid may be defined as a compound of hydrogen and oxygen, and a "third element," usually non-metallic, that may be said to characterize the molecule. (Sulphur may take the place of

oxygen in these compounds, and the acids are called sulph-acids.) Here we have to consider what varies in this class of molecules. It is noticed that hydrogen and oxygen are common to all of them, therefore this "third element" might be supposed to name the compounds; but it is also true that the number of atoms of oxygen varies in many cases; or there is more than one combination of these elements known. The "third element" does not usually vary in the number of atoms in the molecule. The name, in all cases, is formed from the name of the "third element" by means of suffixes and prefixes which vary in form to indicate the amount of oxygen present in the molecule. If but one combination is known, the suffix "ic" replaces the last syllable of the name of the "third element." Thus,  $\text{H}_3\text{BO}_3$  is boric (boron) acid. If two combinations of the same atoms are known, the one containing the less oxygen is named by using the suffix "ous" in the same manner as the suffix "ic" is used; e.g.  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , are sulphurous and sulphuric acid, respectively. If there are three combinations known, the molecule containing the least oxygen is named by using the prefix "hypo" and the suffix "ous" with the name of the "third element"; e.g.  $\text{HNO}$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , are hyp-nitrous, nitrous, and nitric acid, in the order named. If there are four such combinations known, the molecule containing the most oxygen is named by using the prefix "per" and the suffix "ic" in the usual manner; e.g.  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ , are hypochlorous, chlorous, chloric, and perchloric acids, in the order named.

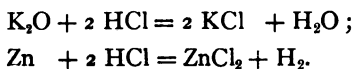
2. *Bases*. — A base is a compound of oxygen and hydrogen with a "third element" called a metal. The question "what is a metal?" is not easily answered; that is, any definition that will include certain elements would exclude others that are commonly classed as metals. It is quite common to divide all elements into acid-forming elements and base-forming elements; but under certain conditions (depending generally on the amount

of oxygen in the molecule) base-forming elements behave like acid-forming elements, and *vice versa*. For the present purpose, however, our knowledge of the bases sodium and potassium will give a sufficiently clear idea of the basic element.

Another fact in connection with bases is that the oxygen and hydrogen are always in the proportion of one atom of hydrogen to one atom of oxygen, or of 1 to 16. If a greater amount is present in the molecule, it is always a simple multiple of these quantities. This group, OH, is called hydroxyl, and forms a part of all bases. These molecules or compounds are called hydroxides. The name of the metallic element united with the word *hydroxide* always names the base; e.g. KOH, NaOH, are potassium and sodium hydroxides, respectively. If more than one combination of the metal and hydroxyl is known, the suffixes "ous" and "ic," less and more, are used in the same manner as is explained under the naming of salts.

3. *Naming of Salts*. — A salt may be defined as a compound formed from an acid by the replacement of its hydrogen, or a part of it, by some metal; e.g. the salts KCl, NaBr, correspond to HCl and HBr. The name of the salt is formed from that of its corresponding acid by changing the terminations as follows: "ic" is changed to "ate," and "ous" into "ite." The name of the metal is added to the name thus formed; e.g. HNO<sub>3</sub> is nitric acid; KNO<sub>3</sub> is potassium nitrate. A metal that forms more than one hydroxide may form more than one salt with the same acid. Such salts are distinguished by adding the suffixes "ous" and "ic" to the metal; as FeCl<sub>2</sub> and FeCl<sub>3</sub> are called ferrous and ferric chlorides, in the order named.

We have seen that a salt is formed by the action of an acid on a base. A salt may also be formed by the action of an acid on an oxide or on a metal.



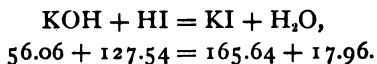
**Molecules, Reactions, and Chemical Equations.** — We have already seen that the formula of a molecule represents, or shows, of what atoms it is composed. An additional fact in reference to them is now particularly emphasized; that is, they represent definite quantities of the elements that enter into them. For example, KOH means that 39 parts or units of mass of potassium, 16 parts of oxygen, and 1 part of hydrogen form the molecule, or that the molecule weighs 56.06 units of mass. All the other formulæ determined represent similar quantitative notions based on exact chemical analysis. The chemical unit of mass is therefore the molecule. This molecule can be changed by changing the atoms that make it up; that is, these atoms may be changed, as to kind, number, and relation to each other in the molecule. (Are there any other changes possible?) These changes are called reactions. A chemical reaction is, therefore, any chemical change taking place among the atoms that form molecules. In general, the change ( $\alpha$ ) may take place in a single molecule; *e.g.* when mercury oxide ( $\text{HgO}$ ) is heated above red heat.

( $\beta$ ) By the action of one molecule on another, as when HCl is brought in contact with KOH.

Why should one molecule react with another? Suppose that each element under the same conditions had exactly the same chemical affinity for every other element that each of the other elements has for it. Would this fact affect the chemical action? It is perhaps sufficient to say that chemical action is an equilibrating of chemical affinities under the conditions imposed. Of course, we know already that heat may apparently destroy chemism; *e.g.* when water is heated to  $2500^{\circ}$ , mercuric oxide to red heat, etc.

Now since reactions are always molecular, what is true of these changes must be true of any mass change. We can go a step further, applying the law of indestructibility of matter, and say that the sum of the masses entering into a reaction must

equal the sum of the new masses produced by this reaction. This is the fundamental idea of a chemical equation. A chemical equation says, therefore, that the mass of the molecules that enter into a chemical change, commonly called the factors, equals the mass of the molecules produced by the reaction, called the products.

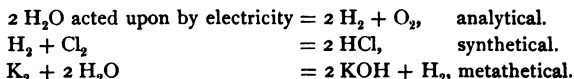


It has been shown that the molecule of potassium hydroxide weighs 56.06 units ; that of hydrogen iodide, 127.54 units ; that of potassium iodide, 165.64 units ; and that of water, 17.96 units. (Notice that here but one unit of mass is used, and that the mass of one atom of hydrogen, as though we should express all mass in milligrammes instead of using kilogrammes, etc.) It is also noticed that the masses reacting preserve the molecular proportions ; e.g. 56.06 units of potassium hydroxide unite with 127.54 units of hydrogen iodide. This unit may therefore become, in practice, grammes, centigrammes, kilogrammes, etc., since these units, grammes, etc., are always equal under the same conditions. In the same reaction, however, the unit of mass must be the same throughout. For example, if one quantity is expressed in grammes, then all the others must be so expressed.

Again, it has been established that a gaseous molecule may be taken as a unit of volume ; hence in reactions between such molecules the equation showing the reaction not only shows the quantitative relation, but measures the volume relation. For example,  $\text{H}_2 + \text{Cl}_2 = 2 \text{HCl}$  says that 1 vol. of hydrogen + 1 vol. of chlorine = or produces 2 vols. of hydrogen chloride.

**Classification of Reactions and Equations.** — The terms *analysis* and *synthesis* have already been defined. If the conception there learned be applied to molecules, it can readily be seen that these reactions refer to changes in a single molecule ;

that is, in analysis, the changing of a more or less complex molecule into simpler ones; and in synthesis, the forming of simple molecules into more complex ones. One is combination, and the other is decomposition. The latter usually requires some other form of energy than chemical energy as such, as heat and electricity. There is still another kind of reaction in which two or more molecules exchange atoms, forming two or more other molecules. Here there are at least two molecules decomposed by the action of one on the other, with or without the aid of heat. Such a decomposition or transposition is called metathesis. Reactions and equations are therefore classed as analytical, synthetical, and metathetical. They are illustrated as follows:—



#### HYDROGEN DIOXIDE (OR DI-HYDROXYL).

**Method of Preparation.**—Hydrogen dioxide is practically or wholly a laboratory product. It is said that small quantities may be found in the air, in rain, and in snow. The compound is generally prepared by treating barium dioxide ( $\text{BaO}_2$ ) with dilute hydrochloric acid or with dilute sulphuric acid. It can also be made by passing carbon dioxide ( $\text{CO}_2$ ) through water in which is suspended barium dioxide.

**Preparation.**—Place 10 g. of barium dioxide ( $\text{BaO}_2$ ) in 20 cc. of water and allow it to stand for fifteen minutes. To this add slowly cold dilute sulphuric acid (1 cc. of acid to 10 cc. of water, or dilute hydrochloric acid, 1 vol. of acid to 3 vols. of water) as long as any precipitate is formed. The beaker in which the action takes place should be kept cold by surrounding it with pounded ice and salt to prevent decomposition of the hydrogen dioxide. When the white precipitate, which is



barium sulphate ( $\text{BaSO}_4$ ), has settled, decant the clear liquid. The liquid is a dilute solution of the dioxide, and in this condition it is studied. The solution should be at most but slightly acid.

**Experimental Study No. 21.** — (a) A dilute solution of potassium iodide ( $\text{KI}$ ) is treated with a few drops of the hydrogen dioxide solution. What change occurs? Prove what the substance is that is set free. What other substances produce the same result? Test this solution with litmus paper. What does this show? For this test the solution of the dioxide must be neutral or nearly so.

(b) Warm 20 cc. in a test-tube, first adding a few grammes of manganese dioxide ( $\text{MnO}_2$ ) and a few drops of sulphuric acid. Prove what gas escapes. Test it with the glowing match.

(c) To 10 cc. of the solution add 1 cc. of ether and 1 cc. of potassium dichromate solution, and shake. Allow it to stand for some time. This action is characteristic of hydrogen dioxide.

(d) With a blunt stick dipped in hydrogen dioxide solution, write (or draw a figure) on a piece of lead sulphide paper. (The paper is made by dipping a piece of filter paper in a dilute solution of lead acetate and exposing it to hydrogen sulphide gas [see page 118]. Dry the paper, and it is ready for use.) This result is quite characteristic, but is not a very delicate test. (What is a delicate test?)

(e) Prepare hydrogen from zinc and sulphuric acid, and when ready ignite the gas as it escapes from the jet. Have ready 10 cc. of pure water in an evaporating-dish, and direct the jet of burning gas against the surface of the water. Continue from five to ten minutes. Test the water for hydrogen dioxide. Explain the change.

(f) Add to 10 cc. of a cochineal solution some of the dioxide solution. How does this action compare with the action of chlorine in the same solution? What is the active agent? Compare with (b).

**Physical Properties.** — Owing to the difficulty of obtaining pure hydrogen dioxide, its physical properties are not wholly known. It can be obtained nearly free from water as a somewhat syrupy, colorless liquid, heavier than water. A method of obtaining it quite free from water is to subject it to a low temperature,  $-25^{\circ}$  to  $-30^{\circ}$ ; when the water solidifies, the dioxide remains a liquid. It cannot be vaporized, so that its vapor density cannot be determined. A portion, however, vaporizes in a vacuum. The liquid has a specific gravity of 1.45. It begins to decompose at  $15^{\circ}$ , and at  $100^{\circ}$  the decomposition takes place very rapidly.

**Chemical Properties.** — This compound is very unstable, decomposing into water and free oxygen gas. It is soluble in ether and in water. It is a very active agent, chemically speaking. It bleaches many colored compounds because of the oxygen given off in the nascent state. It sets iodine free from potassium iodide (KI), much resembling ozone in its action. It readily gives up oxygen to such metals as silver and platinum, which are not at all acted upon by ordinary free oxygen. It changes lead sulphide (PbS) to  $\text{PbSO}_4$  (lead sulphate, a white compound).

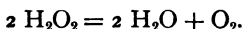
**Tests.** — The solution supposed to contain the dioxide is slightly acidulated with sulphuric acid, and a few drops each of ether and a solution of potassium dichromate are added, and the mixture shaken. The ether rises to the top, colored blue. The color is due to the solution of a compound of chromium, which is formed by the reaction.

**History and Uses.** — This compound was discovered by Thenard in 1818. It has, however, only recently become of practical importance. It is now made on the commercial scale. It is used for bleaching such substances as ostrich feathers, hair, wool, silk, and whalebone. It is claimed that it is useful for medicinal purposes. It is used to restore oil paintings that have become blackened by exposure to air containing hydrogen

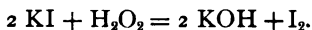
sulphide. The pigments used in the painting often contain compounds of lead with other elements; e.g. lead carbonate ( $\text{PbCO}_3$ ). This latter compound forms in the air lead sulphide ( $\text{PbS}$ ), which is black. The hydrogen dioxide changes the sulphide to the sulphate, which is white.

**Formula for the Molecule.**—When hydrogen dioxide is analyzed, it is found to contain 94.12 per cent of oxygen and 5.88 per cent of hydrogen, or 1 part of hydrogen to 16 parts of oxygen, or 2 parts of hydrogen to 32 parts of oxygen. The formula may be, therefore,  $\text{HO}$ , or any multiple of this. The gas density of the compound has not been determined, and consequently its formula cannot be established in this manner. The proportion of oxygen to hydrogen in water is 8 : 1 or 16 : 2. There is, therefore, relatively twice as much oxygen in this compound as there is in water. When there are two atoms of hydrogen there are two atoms of oxygen. The action of this compound when decomposed points strongly toward the formula  $\text{H}_2\text{O}_2$  or  $\text{HO}-\text{OH}$ , dihydroxyl.

The amount of oxygen, by volume, given off from a definite mass of the dioxide is a little less than what theory would show should be the amount, provided the molecule is  $\text{H}_2\text{O}_2$ . But it is very difficult to prepare absolutely pure hydrogen dioxide. The reaction of decomposition may therefore be represented—



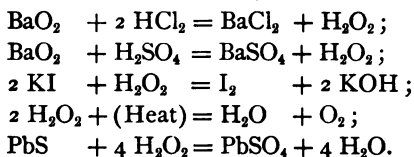
Again, when potassium iodide ( $\text{KI}$ ) is treated with the dioxide solution, the action is—



Here the oxygen is set free and unites with the potassium of the potassium iodide ( $\text{KI}$ ), setting the iodine free, forming  $\text{K}_2\text{O}$ , but in the presence of water that is formed this becomes  $2 \text{KOH}$ . When ordinary oxygen is passed through a solution of  $\text{KI}$ , it produces no change. When the hydrogen dioxide was

heated, it gave off free oxygen, and water was formed. Now if the molecule is  $\text{H}_2\text{O}_2$ , one molecule will furnish one molecule of water and one atom of oxygen; that is, the oxygen escapes atom by atom. Under these conditions oxygen is more active chemically; another illustration of the fact that an element is more active chemically in the nascent state than in its ordinary free condition.

Some of the reactions produced during the study of the dioxide are as follows:—



What was the proof of the presence of an alkali?

## SULPHUR.

**Occurrence and Distribution.**—Sulphur is found in nature in both the free and the combined condition. In the free condition it is found in the vicinity of volcanoes. It occurs here in rhombic crystals and in crystalline masses mixed with gypsum and other earthy matter. The principal localities for native sulphur are in Sicily, Spain, Italy, and California.

Combined sulphur is found widely distributed, combined with a large number of different metals; in fact, nearly every metal is found in nature thus combined. Sulphur occurs combined with hydrogen, oxygen, carbon, and often with nitrogen, in vegetable substances such as the white of an egg, mustard oil, bile, etc.

**Method of Preparation of Sulphur from the Native Deposit.**—Nearly all the sulphur of commerce is taken from Italy and Sicily. The sulphur occurs in beds or layers, surrounded by and mixed with marl, limestone, and gypsum. These masses are broken up into small pieces and placed in pits dug in the ground or in special chambers. Air passages are left in the pile of ore, and the sulphur is ignited. The burning produces heat sufficient to melt the unconsumed sulphur, which gathers on the bottom of the pit free from a large percentage of its impurities. This product is called crude sulphur. The crude sulphur is further purified by distillation. From the crude sulphur two products are prepared, called the "flowers" of sulphur and brimstone or brennestone.

**Experimental Study, No. 22. — 1. Study of its Forms.**—Materials used are flowers of sulphur and brimstone.

(a) Treat about  $1\frac{1}{2}$  g. of flowers of sulphur with 5 to 10 cc. bisulphide of carbon. (Do not use the bisulphide of carbon near the burning lamp.) Close the tube and shake, allowing it to stand for ten minutes. Pour off the clear solution into a beaker, and let the carbon disulphide evaporate spontaneously.

(b) Take 1 g. of the powdered brimstone and treat in the same way, adding an excess of carbon disulphide. Examine and compare the crystals with those produced under (a). What does the result show in reference to the flowers of sulphur? Is there more than one kind of sulphur in flowers of sulphur? If necessary, use a hand magnifier with which to examine the crystals.

(c) Take a clay pipe, or small clay crucible, and fill with sulphur; cover, and carefully fuse, adding sulphur until the crucible is full. Allow this to cool slowly, and when the crust just covers the top, make a hole in it and quickly turn out the remaining liquid sulphur. Compare the crystals thus formed with those made under (b). Describe their form, pointing out

any differences that may be discovered. Examine these same crystals three or four days later.

(*d*) Dissolve some flowers of sulphur in a fairly concentrated potassium hydroxide solution. Boil the mixture, if necessary, to dissolve the sulphur. Filter, if not clear, and add hydrochloric acid. Try to filter. Explain the result. Examine this and the flowers of sulphur under the microscope.

(*e*) Take 10 g. of sulphur and place in a large test-tube; heat slowly until the sulphur is fused. Notice the color, mobility, and, if possible, determine the temperature to which the mass is subjected. Now heat, applying the flame along the length of the tube containing the sulphur, noticing, at least, color and mobility. Continue the heat until the sulphur begins to escape in the form of a vapor. Carefully observe all changes as the temperature rises. Next pour the liquid sulphur into a beaker which is nearly full of cold water. When cool enough, remove the sulphur from the water and examine it, comparing it with the forms just studied.

(*f*) Heat 5 g. of sulphur until it is just liquid and pour it into water. Compare with (*e*). Leave (*e*) for a few hours and then make the comparison.

(*g*) Treat a bit of the plastic sulphur with bisulphide of carbon. Does it dissolve?

(*h*) The chemical relation of sulphur to oxygen and the chlorine group has already been determined. Mix 2 g. of sulphur with 4 g. of copper filings and heat them in a tube until chemical action begins, when the tube should be removed from the flame and the effect of the chemical action observed. Again, heat 2 g. of sulphur in a tube until sulphur vaporizes, holding a thin strip of copper in the vapor. At what temperature did the action begin?

(*i*) Rub a bead of mercury and a small amount of sulphur in a mortar.

(*j*) Treat  $3\frac{1}{2}$  g. of iron filings and 2 g. of sulphur, intimately

mixed, as copper and sulphur were treated in (h). Examine the residue. Treat a portion of the residue with hydrogen chloride. Notice the odor of the gas escaping.

(k) Fuse a bit of sulphur with sodium carbonate on charcoal. Remove the residue and moisten the mass and place it on a silver coin. This result is characteristic of sulphur. What is this black product on the silver?

**Physical Properties.**—Sulphur is a solid at ordinary temperature and exists in three forms; namely, the amorphous, the crystalline, and the plastic forms. Only one variety is found in nature and it is crystallized in yellow rhombic octahedrons. The same form is produced when sulphur is dissolved in carbon disulphide and is allowed to crystallize from this solution. The crystals are brittle and easily electrified. Sulphur is insoluble in water, but the crystalline variety is very soluble in carbon disulphide.

Another variety of sulphur is seen in the crystals formed from fused sulphur. These crystals are yellowish brown and belong to what is called the monoclinic system of crystals. Their specific gravity is 1.96, while the common sulphur has a specific gravity of 2.05. It is insoluble in carbon disulphide. These crystals melt at  $120^{\circ}$ , while the common form melts at  $112^{\circ}$ . It changes to the first variety slowly at ordinary temperatures, but quite rapidly as the temperature rises.

When sulphur is heated to a temperature of  $112^{\circ}$ , it fuses and becomes a yellow colored liquid. If it is heated to higher temperatures, it undergoes changes in color and mobility. At  $250^{\circ}$  it becomes a stiff, pitchy-appearing substance. At  $440^{\circ}$  it becomes a thin liquid and boils. If it be suddenly cooled down from any temperature above  $250^{\circ}$ , it becomes a soft, plastic, and elastic mass. This mass is insoluble in carbon disulphide. It soon begins to harden, and in a few days has changed to the ordinary variety.

The milk of sulphur (or *lac sulphuris*) is also amorphous,

but slowly passes into the common form. The chemical properties of the crystalline varieties are the same. (Compare oxygen and ozone with it.)

Sulphur boils at  $440^{\circ}$ , and at a temperature not far from  $500^{\circ}$  its vapor density is 96. If the temperature is made higher, the density decreases, and at  $860^{\circ}$  it becomes constant at  $32^{\circ}$ , remaining so until the temperature of at least  $1000^{\circ}$  is reached.

**Chemical Properties.** — At ordinary temperatures sulphur is not chemically active. We have noticed that it unites with the metals at high temperatures, and in many other ways it resembles oxygen. It sometimes replaces oxygen in certain of its compounds. Its union with the metals, copper, iron, and mercury, is, generally speaking, typical of its general activity. It unites with most of the non-metallic elements at high temperatures, — *e.g.* with oxygen at  $260^{\circ}$ , — but when the action begins, it continues without further addition of heat.

**Tests.** — Free sulphur is tested for by fusing it on charcoal with sodium carbonate. Sodium combined with sulphur forms sodium sulphide ( $\text{Na}_2\text{S}$ ). This sulphide produces a black spot of silver sulphide ( $\text{Ag}_2\text{S}$ ) when placed on a silver coin. Its physical properties of volatility, odor when burned, color, etc., make it easily recognized.

**History and Name.** — Sulphur has been known from the earliest time, either under the name *sulphur* or *brennestone*. The symbol is S.

**Uses.** — Sulphur is used in making matches, vulcanized rubber, gunpowder, fireworks, and also in many compounds, such as sulphuric acid. It is used in medicine under the names milk of sulphur (*lac sulphuris*) and flowers of sulphur. It is also used in bleaching straw, wool, and silk goods.



*Compound of Sulphur and Hydrogen.*

**Occurrence and Distribution.** — Hydrogen sulphide is found in nature, in volcanic regions, in the gases escaping from the sides of the volcano, and in certain natural waters called sulphur waters. It is also formed when certain organic compounds containing sulphur decay, as, for example, in decayed eggs.

**Methods of Preparation.** — Although this compound occurs in nature it is artificially made for purposes of study and other uses. It has been seen that of the elements studied thus far, most of them unite readily with hydrogen, either at ordinary temperatures or at slightly raised temperatures. But sulphur and hydrogen do not unite short of red heat. If hydrogen is mixed with sulphur vapors and passed through a red-hot tube filled with small pieces of pumice stone or brick, the union of the two elements takes place. However, only a portion of the hydrogen unites with the sulphur, showing that it has a much less affinity for hydrogen than it has for oxygen. It is commonly prepared by the action of hydrogen chloride or of sulphuric acid, on the sulphide of some metal; e.g. ferrous sulphide, represented by the formula  $\text{FeS}$ .

We have seen how the metals sodium and potassium replace the hydrogen of hydrogen chloride. Other metals, like iron, will act in the same way; that is, although chlorine has a great affinity for hydrogen, it will in most cases readily exchange it for a metal.

**Preparation.** — Five grammes of sulphide of iron are placed in the generating-bottle, fitted up as it is for preparing hydrogen, about 20 cc. of water are added, and then concentrated hydrochloric acid or sulphuric acid is slowly poured in. The generator is meanwhile shaken till the gas escapes freely. Too much sulphuric acid prevents action. Why?

Collect the gas over water and in as many bottles as is

needed ; also pass the gas into 60 cc. of water until the latter is saturated.

**Experimental Study, No. 23.** — (a) Take a bottle of gas and turn in 100 cc. of water, close tightly with solid rubber stopper, and shake, opening the bottle with the mouth under water. Note result. Explain.

(b) Invert a bottle of hydrogen sulphide over a bottle of air, and allow it to stand for a short time. Examine the lower bottle of gas for hydrogen sulphide with a burning stick. See under chemical properties (c). What does this result show?

(c) Pass the gas through a tube heated nearly to redness. Examine the escaping gas. What is the deposit on the tube? Explain.

(d) Test the contents of the bottles with moist litmus paper.

(e) Examine a bottle of the gas with a lighted stick. Explain the deposit on the bottle. For which has oxygen the greater affinity, sulphur or hydrogen? How does the temperature of the action affect the result?

(f) Dry the gas by passing it through a "calcium chloride tube," and when escaping rapidly from the jet, ignite it, and hold over the flame a cold beaker. What is the liquid on the sides of the beaker? Test it with litmus paper.

(g) Invert a bottle of the gas over a bottle of dry chlorine gas. After the reaction test the contents of the bottle with litmus. To what is the action due? What is the deposit in the bottle? Explain why there is a deposit.

(h) Allow the gas to escape against a piece of bright copper or silver. Compare the result with the action of sulphur on these metals.

(i) Prepare solution of salts of the following metals : copper, arsenic, antimony, and lead. Place about 10 cc. of each solution in separate test-tubes. Add a few drops of hydrochloric acid to each tube, and then add the water solution of the gas, or pass the gas into the solution. What are the compounds formed?

(j) Allow the water solution of the gas to stand for a day or so. Prove what the white residue is. There is free oxygen dissolved in the water. Explain how the presence of this oxygen might cause the change.

(k) Moisten a piece of filter paper with lead acetate solution, and allow the gas to escape against it. This is a characteristic test for the compound.

**Physical Properties.** — Hydrogen sulphide is a gas at ordinary temperatures and pressures, but it can be converted into a liquid which boils at  $-62^{\circ}$  and becomes a solid at  $-85^{\circ}$ . It is a colorless gas and has a characteristic odor often compared with that of rotten eggs; in fact, the odor of decaying eggs is largely due to this gas. Its density is 17, therefore it is heavier than the air. It is soluble in water, 1 vol. of water dissolving about 3.5 vols. of the gas at ordinary temperatures, but if the solution is left in an unstoppered bottle, the gas slowly escapes. It readily escapes if the solution is boiled.

The gas is decomposed by heat at temperatures of about  $400^{\circ}$ . The pure gas is a narcotic poison, but when mixed with the air it is both a narcotic poison and an irritant producing headache and nausea. Five or six per cent of it in the atmosphere is sufficient to produce symptoms of poisoning if breathed for some time. The best remedy is to inhale and exhale rapidly pure air, filling the lungs completely at each respiration. This gas often escapes with sewer gases in dwellings, with great injury to the health of the inmates.

When the gas is brought in contact with the air at raised temperatures, it is decomposed, and the elements unite with oxygen, water and sulphur dioxide ( $\text{SO}_2$ ) being formed. When the temperature of the flame is reduced, or the supply of oxygen is limited, the sulphur is in part deposited, showing the greater affinity of oxygen for hydrogen, or that the latter union takes place at a lower temperature. The water solution of the gas is acid to litmus paper. The solution decomposes slowly, de-

positing sulphur, the hydrogen uniting with the oxygen, which is dissolved in the water to form water. Chlorine gas decomposes hydrogen sulphide, forming hydrogen chloride, and sulphur is deposited. Bromine and iodine will also set sulphur free, forming the hydrogen compounds of these elements. In fact, this latter reaction furnishes a practical method of preparing these two compounds. Many metals decompose hydrogen sulphide at ordinary temperatures ; *e.g.* copper, silver, lead, etc. When solutions of compounds containing such metals are treated with this gas in the form of a water solution, or by passing the gas through the solution, a mutual decomposition and transfer of elements occurs, the sulphide of the metal being formed, the hydrogen taking the place of the metal.

*Determination of the Molecular Formula of the Compound Hydrogen Sulphide.*

It is assumed that it is known that the compound contains only hydrogen and sulphur, since it can be prepared directly from the pure elements hydrogen and sulphur.

**Quantitative Composition. — Experimental Study, No. 24. —** A tube like Fig. 9 is arranged for collecting gases over mercury, and is partly filled with dry hydrogen sulphide gas, the volume of which is accurately known. A piece of tin is placed in the upper part or closed end of the tube. This end of the tube is now heated. The sulphur slowly unites with the tin, forming sulphide of tin, a solid, the volume of which is relatively very small. It will be found that the gas remaining in the tube is pure hydrogen, the volume of which is equal to the volume of the hydrogen sulphide decomposed.

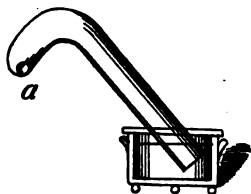


FIG. 9.

Suppose, for example, that 100 cc. of gas had been used, and to simplify the calculation that its volume is taken at  $0^{\circ}$  and under one atmosphere of pressure. Then, since the density of the gas is 17, the 100 cc. will have a mass represented by the following : —

$$17 \times .0896 \times .1 = .15232 \text{ g.}$$

Now since the volume of hydrogen is equal to that of hydrogen sulphide, there are 100 cc. of hydrogen gas which under the same conditions will weigh .00896 g. The per cent of hydrogen is, therefore, 5.88 +. Since the remainder of the compound is sulphur, it must form 94.12 + of the original compound. (The sulphur of hydrogen sulphide may be set free by chlorine gas acting on the compound, when it can be weighed. When examined in this manner, it is found to consist of 94.12 per cent of sulphur.)

The facts for the determination of the formula of this compound are, therefore : —

(a) That the compound consists of 5.88 + per cent of hydrogen, and of 94.12 + per cent of sulphur.

(b) That the density of the gas is 17.

(c) That 1 vol. of the gas yields 1 vol. of hydrogen.

(d) That no compound known contains a less proportion of sulphur.

**Conclusions.** — From Avogadro's law it is concluded that the molecule of the gas has a mass of 34, 5.88 per cent of which is hydrogen and 94.12 per cent is sulphur. Therefore in this molecule there are 2 parts of hydrogen and 32 parts of sulphur.

From the fact (c) there is the same number of molecules of hydrogen set free as there are of molecules of the hydrogen sulphide. But a molecule of hydrogen consists of two atoms, and hence there are two atoms in this molecule. Since the sulphur in this molecule is the smallest found in any molecule, this mass

is an atom. The atomic mass of sulphur is, therefore, 32. The formula for the compound is  $H_2S$ .

**Supposed Cause of Allotropism in Sulphur.** — As has been pointed out, the vapor density of sulphur at  $500^\circ$  is 96, decreasing as the temperature rises until at  $860^\circ$  to  $1040^\circ$  it becomes constant at 32. At this temperature there are, therefore, two atoms to the molecule, the atomic mass being 32. At  $500^\circ$  there are six similar atoms in the molecule, according to the same method of reasoning. The allotropism of sulphur appears to be due to molecular concentration, as was the case with oxygen. There is no positive knowledge as to the number of atoms in the molecule of solid or of liquid sulphur. Reasoning from analogy, it is inferred that the same causes produce the allotropism of sulphur that produce it in oxygen. The chemical characters of the crystalline varieties of sulphur are practically identical. This suggests a difference in molecular arrangement, since crystalline form is probably due to molecular arrangement.

**History and Name.** — The name *hydrogen sulphide* is given according to the nomenclature of binary compounds. It is also called hydrosulphuric acid, since it gives an acid reaction in its water solution; and further, its hydrogen can be replaced by metals. It is sometimes called sulphuretted hydrogen. It was known in the sixteenth century, but its composition was not understood. In 1777 Scheele studied its properties, and showed that it could be formed by heating sulphur in hydrogen (inflammable air).

**Uses and Tests.** — Hydrogen sulphide is used principally as a reagent in qualitative analysis. It is a poisonous substance. Taken internally in small doses, however, it is regarded as a medicine. The so-called sulphur waters are supposed to owe their medical properties to the presence of this gas in the water.

It is tested for by wetting pieces of filter paper in a solution of a compound containing lead (*e.g.* lead acetate), and exposing this paper to the action of the gas. Black sulphide

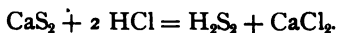
of lead (PbS) is formed. What previous chemical action is similar to this?

#### REACTIONS PRODUCED IN THE STUDY OF HYDROGEN SULPHIDE.

$\text{H}_2 + \text{S}_2 = ?$	Complete, and read by mass and volume.
$\text{FeS} + \text{HCl} = \text{FeCl}_2 +$	Complete, and read by molecule and mass.
$\text{FeS} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 +$	" " " "
$\text{H}_2\text{S} + \text{Heat} = ?$	" " " "
$\text{H}_2\text{S} + \text{O}_2 = \text{SO}_2 +$	" " " "
$\text{H}_2\text{S} + \text{Cl}_2 = ?$	" " " "
$\text{H}_2\text{S} + \text{Sn} = \text{SnS} +$	" " " "

#### HYDROGEN DISULPHIDE.

Hydrogen disulphide is supposed to have the formula  $\text{H}_2\text{S}_2$ . It is analogous to hydrogen dioxide. It is a very unstable compound, and a liquid of a yellow color and an unpleasant odor. It slowly decomposes at ordinary temperatures into hydrogen sulphide and sulphur. Regarded as analogous to hydrogen dioxide, it may be represented by the formula  $\text{H}-\text{S}-\text{S}-\text{H}$ . It can be prepared by treating calcium disulphide with hydrochloric acid:—



#### *Compounds of Sulphur with the Members of the Chlorine Family.*

Sulphur forms compounds with all the members of the chlorine family, but they are all unstable and are generally of interest from a purely chemical standpoint only. Sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ) is used in vulcanizing rubber. This is the most stable of these compounds. It can be distilled without decomposition as a yellow liquid, boiling at  $138^\circ$ . It readily decomposes in contact with water. What will become of the chlorine? Why?

The formulæ of some of the other halogen compounds are  $\text{SCl}_2$ ,  $\text{SCl}_4$ ,  $\text{S}_2\text{Br}_2$ ,  $\text{S}_2\text{I}_2$ ,  $\text{SI}_4$ .

**Problem.** — The density of one of the compounds of sulphur and chlorine is 67.37; it contains 47.483 per cent of sulphur and 52.517 per cent of chlorine. The atomic masses of the elements being known, determine the formula of the compound.

---

## SELENIUM.

**Distribution and Occurrence.** — The element *selenium* occurs associated with sulphur in certain minerals containing the metals copper, lead, and silver. It is, however, chiefly combined with lead. It is also found in small quantities in certain natural deposits of sulphur. It occurs usually in chemical combinations, but has been found free.

**Preparation.** — Selenium is prepared from the deposits on the walls of the lead chambers used in making sulphuric acid, or from the dust that settles in a chimney used for roasting iron pyrites. The selenium is set free by first fusing these deposits with sodium nitrate and carbonate, the former of which furnishes it with oxygen, thus forming a soluble compound of selenium, oxygen, and sodium, called sodium selenate ( $\text{Na}_2\text{SeO}_4$ ). The fused mass is treated with water, which dissolves the selenium compound, and this solution is acted on by some agent that removes the oxygen, setting the selenium free. Sulphur dioxide ( $\text{SO}_2$ ) is usually used.

**Properties.** — Selenium is a solid at ordinary temperatures, and exists in two allotropic forms, thus resembling sulphur. These forms differ in color, solubility, and specific gravity. At  $700^\circ$  it is converted into gas, having a density at  $1400^\circ$  of 79. It very closely resembles sulphur in its chemical properties, although it is less active. It unites with the oxygen of the air



at raised temperatures, producing a gas of very disagreeable odor, often compared to that of decaying horseradish.

**History and Name.** — This element was discovered in 1817 by Berzelius, in the deposits formed in the lead chambers of a sulphuric acid factory located at Gripsholm. The name *selenium* is derived from the Greek word for moon, and was probably suggested by the fact that another element greatly resembling it in its properties, discovered in 1798, had been called *tellurium*, from *tellus*, the earth. It is used in studying light and electricity.

#### *Compound of Selenium and Hydrogen.*

The methods of preparing this compound are similar to those used in preparing hydrogen sulphide; *e.g.* by heating hydrogen and the vapor of selenium together, or by treating selenide of iron ( $\text{FeSe}$ ) or potassium selenide ( $\text{K}_2\text{Se}$ ) with hydrochloric acid.

**Properties.** — Hydrogen selenide is a gas and possesses a remarkably disagreeable odor; in general, resembling hydrogen sulphide. The density of the gas is 40.5. Its properties are analogous to those of hydrogen sulphide.

**Formula of the Compound and the Atomic Mass of Selenium.** — When hydrogen selenide is heated with tin in a tube like the one used in decomposing hydrogen sulphide, it is decomposed, and pure hydrogen is left with the solid selenide of tin. The volume of the hydrogen is the same as the original volume of the gas.

One hundred cubic centimetres of the gas will therefore yield how much hydrogen by mass? How much selenium? How much does the 100 cc. of gas weigh?

From the following facts show why the formula is  $\text{H}_2\text{Se}$  and that the atomic mass of selenium is 79: —

(a) The compound consists of 2.47 per cent of hydrogen and 97.53 per cent of selenium.

(b) The density of the gas is 40.5.

(c) The volume of hydrogen in any given volume of the gas is equal to that of the original gas.

(d) This amount of selenium is the smallest found in any molecule containing it.

**The Elementary Molecule.** — Since the density of selenium is 79, its molecular mass is 158, and since its atomic mass is 79, there must be at least two atoms to the molecule. The molecule is therefore represented by  $\text{Se}_2$ , Se being the symbol for selenium.

Selenium forms compounds with the chlorine group more stable than are the corresponding compounds of sulphur.

---

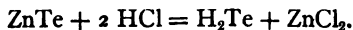
## TELLURIUM.

**Occurrence and Distribution.** — This element is found in nature in but few localities, the principal ones being in California and Hungary. It was first discovered in gold ore, but is, however, found with silver, lead, and bismuth ores. It is rarely found free.

**Properties.** — Tellurium is a solid, having a metallic lustre and a bluish white color. It can be converted into a vapor having a density of 125. As a solid it is brittle, melts at  $500^\circ$ , and has a specific gravity of 6.24. In general, its physical properties are those of a metal. It has chemical properties much resembling those of sulphur and selenium.

### *Compound of Tellurium and Hydrogen.*

**Preparation.** — This compound can be made by heating the element with hydrogen gas. It is usually formed from a telluride of some metal like zinc ( $\text{ZnTe}$ ) by the action of hydrochloric acid. The reaction is similar to that occurring when hydrogen sulphide is prepared.



**Properties.** — This compound is a gas with an odor resembling that of hydrogen sulphide, but far more disagreeable. In general it resembles the hydrogen compounds of sulphur and selenium. Its density is 65. It can be shown to contain the same quantity of hydrogen as the volume of gas decomposed. Therefore there is a molecule of hydrogen in the molecule of the hydrogen telluride. It is also known that 1 part of hydrogen unites with 62.5 parts of tellurium; therefore its formula is  $H_2Te$ , and the atomic mass of tellurium is 125.

Tellurium unites with the chlorine family in a manner similar to that of sulphur and selenium.

### OXYGEN FAMILY.

It is customary to consider oxygen, sulphur, selenium, and tellurium as forming a family or group of elements, because of the great similarity in their physical and chemical properties. This relation, however, is one of gradation of properties, as can be seen by examining the following facts: —

	OXYGEN.	SULPHUR.	SELENIUM.	TELLURIUM.
State of aggregation	Gas.	Solid.	Solid.	Solid.
Character . . . .	"	Non-metallic.	More metallic.	Most metallic.
Density . . . .	16	32	79—	125
Specific gravity . .	1.12 (as liquid)	1.96—2.07—	4.2—4.8	6.2
Melting-point . .	?	114°—120°	217°	500°
Boiling-point . . .	181°	448°	700°	Red heat.
Atomic mass . . .	16	32	79	125(?)

All of the members of the group readily unite with the metals, but the chemical activity decreases as the atomic mass increases.

Hydrogen oxide, or water, is not readily decomposed by heat, requiring temperatures above  $1000^{\circ}$ ; while the hydrogen compounds of the other elements are quite readily decomposed, the necessary temperatures decreasing to tellurium, which requires the lowest temperature.

They all unite with two atoms of hydrogen, and form but one stable compound with it.

Selenium occupies a position between sulphur and tellurium, as is shown by its properties and the atomic mass; *e.g.*

$$32 + 125 = 157. \quad 157 \div 2 = 78.5.$$

It is also to be noticed that the metallic appearance (that is, a physical property) increases from oxygen to tellurium. The chemical properties of tellurium are not those of a metal, however.

**Thermal Facts or Heat of Formation.** — When hydrogen and oxygen unite, forming water, — that is, 2 g. of hydrogen and 16 g. of oxygen, and if the water formed be considered at  $0^{\circ}$ , — then 68,360 calories of heat are given out. At steam temperature 57,200 calories of heat are given out. In the formation of hydrogen sulphide only 4500 calories of heat are given out, while the corresponding compounds of selenium and tellurium absorb heat in their formation, and require the continued application of heat to continue the reaction. Such reactions as the latter are called endothermic, while the former are called exothermic. The exothermic reactions may take place without any application of heat, or at most they only require that the reaction shall be started, when it continues until it is complete. The temperature necessary to keep up the reaction is the result of the reaction. When a compound is decomposed that requires the application of heat for its formation, — that is, heat is absorbed in the formation of the compound, — the corresponding amount of heat is given out, and when the decomposition is once started it continues until completed. Explosive

substances illustrate this kind of decomposition; *e.g.* nitroglycerine; when decomposition is started, even by a concussion, the decomposition continues with explosive results.

It has been shown that oxygen decomposes the hydrides of this group. This is according to the thermal law of "heat of formation," which says that when elements or compounds are brought into conditions necessary for chemical action, the changes will occur which produce the greatest development of heat, provided that no external force is necessary to produce the change. The "heat of formation" means the heat produced when the masses of matter represented by the chemical formula of the compounds produced are made to unite. For example, when 1 g. of hydrogen and 35.37 g. of chlorine unite chemically, 22,000 calories of heat are given out. When iodine and hydrogen unite, heat is absorbed. In every chemical action heat is either absorbed or evolved.

When a compound is decomposed, the heat necessary to do this work or the amount of heat absorbed is just equal to the amount given out when the compound is formed. However, the heat evolved in any chemical action is not directly a measure of the chemism of the atoms that enter into the change, since heat energy is required to separate the atoms of the molecules before the union can take place, and that amount is consequently absorbed. The heat evolved is therefore only a relative measure of the chemism. For example, when hydrogen and oxygen unite, 68,360 calories of heat are set free, but this does not indicate all the heat generated, since the molecules  $H_2$  and  $O_2$  must first be decomposed and this quantity of heat is absorbed. If, therefore,  $x$  represents the amount of heat evolved,  $x_1$  the true amount of heat produced,  $a$  the amount of heat absorbed in the decomposition of the molecule of hydrogen, and  $a_1$  the amount absorbed by the decomposition of a molecule of oxygen, then  $x = x_1 - (a + a_1)$ .

**NITROGEN.**

**Occurrence and Distribution.** — The element nitrogen is widely distributed in nature, both in the free state and in combination. It is an essential element in all animal and vegetable bodies, it being found in protoplasm, the form of matter always present when life is present. It is therefore one of the elements necessary to all perfect plant or animal foods. It is present in a large number of useful manufactured compounds, such as most of the great explosives; *e.g.* nitro-glycerine, dynamite, gunpowder, and guncotton. It is found free in the air, constituting four-fifths of it by volume.

**Methods of Preparation of Nitrogen.** — Since nitrogen exists free in the air, it is only necessary to separate the oxygen to obtain fairly pure nitrogen. We have already found several elements that readily unite with oxygen, such as sulphur, hydrogen, phosphorus, sodium, and potassium. The product of the reaction with phosphorus with the air is a solid, soluble in water, and consequently does not interfere with the remaining gas. Heated copper also readily takes up oxygen from the air, forming copper oxide ( $\text{CuO}$ ), and leaves the free nitrogen. Nitrogen can also be prepared from many of its compounds by heat, and by the action of other elements, or compounds, as when a compound ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ) is heated, or when potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is heated as a dry powder with ammonium chloride ( $\text{NH}_4\text{Cl}$ ).

**Preparation.** — To prepare nitrogen from the air, use a small porcelain crucible, floating it on water by means of a piece of cork. Dry a piece of phosphorus with filter paper and transfer it immediately to the crucible; have ready a bottle that will allow the crucible to enter its mouth, ignite the phosphorus, and place the bottle over the crucible with the mouth under water.

Why do bubbles of gas escape? What are the bubbles? Why does the water rise in the bottle finally?

Again, dry ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ) is placed in a large tube or a 100 cc. flask prepared for collecting gas over water, and is gently heated until the gas escapes with sufficient rapidity, when the heat is lessened, only enough being applied to keep up the flow of gas. (A mixture of potassium nitrite and ammonium chloride can take the place of the ammonium nitrite.)

Another method of preparing pure nitrogen is by using an intimate mixture of 20 g. of potassium dichromate and 10 g. of ammonium chloride. The mixture is heated in a large test-tube or flask, and the gas is collected as before.

**Experimental Study, No. 25.** — (a) Test a bottle of the gas for solubility, specific gravity, and other physical properties.

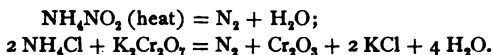
(b) Test a bottle of the gas with a burning stick.

(c) Examine or determine the relation of nitrogen to the elements thus far studied; *e.g.* the elements chlorine, bromine, oxygen, etc.

**Physical Properties.** — Nitrogen is a gas without odor, color, or taste. It is only slightly soluble in water; about 1.5 (1.48) vols. of the gas are dissolved in 100 vols. of water at  $0^\circ$ . It is a little lighter than air, having a specific gravity of .971. Its density is 14.01. It was until the year 1877 classed as one of the permanent gases, but was then condensed into a liquid under a pressure of 280 atmospheres and a temperature of  $-130^\circ$ .

**Chemical Properties.** — Nitrogen can be made to unite directly with oxygen and hydrogen by means of the electric spark, with boron, and a few other elements at high temperature. In general, nitrogen may be said to be indifferent, chemically speaking, towards other elements, and when combinations are made, the compounds are mostly unstable. It has the greatest affinity for hydrogen. The gas is not a poison, but produces death by suffocation when animals are placed in it.

## REACTIONS OCCURRING IN PREPARATION OF NITROGEN.



Balance, and explain on basis of affinities already learned.

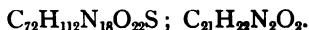
**History and Name.** — The name *nitrogen* is derived from *nitron*, because it is found in nitre, and *genein*, meaning *I produce or form*. It is also called *azote*, a word meaning *without life*, referring to the fact that it does not support life. The latter name was given to it by Lavoisier, who applied the name to air after the oxygen had been removed.

It was discovered in 1772 by Rutherford, a botanist, while experimenting to discover the effect of animal respiration on air. He proved that the remaining gas would neither support life nor ordinary burning.

**Uses and Tests.** — The very inertness of nitrogen makes it useful in determining gas densities, in thermometer tubes, and in many experiments in which it is necessary to have present an inactive gas. Its inactivity serves to distinguish it from other gases, when taken in connection with its physical properties.

*Compound of Nitrogen with Hydrogen.*

**Occurrence and Distribution.** — Judging from the chemical properties of nitrogen, it would not be supposed that its compounds would be found in nature; but through the agency of life nitrogen is built into a large number of compounds, most of them consisting of the elements carbon, hydrogen, oxygen, and nitrogen. Some of the compounds are very complex, — that is, they consist of a large number of atoms and frequently of several kinds of atoms; e.g. such compounds as albumen and strychnine represented, in the order given, by the formulæ





Under the action of heat and other natural agencies nitrogenous organic compounds are decomposed into simpler forms. Under these conditions the nitrogen unites with some of the hydrogen, and the other elements arrange themselves according to their affinities. Certain minute living organisms, generally included under the term *bacteria*, set up this change whenever the organic matter is exposed to their action under the proper conditions. Consequently we should expect to find the hydrogen compound, commonly called ammonia, in air and water quite universally distributed. The ammonia unites with elements and other compounds, and consequently usually exists in combinations; *e.g.* aqua ammonia, ammonium chloride, etc. Ammonia exists in the atmosphere and in soils; the quantity present at any one time is, however, quite small.

**Methods of Preparation.** — Nitrogen may be made to unite with hydrogen by means of the electric spark, the temperature of union being about  $3500^{\circ}$ . By this method only about three per cent can be made to unite unless the ammonia is removed as fast as it is formed. This can be done by allowing the mixture of nitrogen and hydrogen to stand over hydrochloric acid. Its principal source is from the decomposition of organic matter, referred to in the preceding paragraph. When animal matter, such as animal refuse, bone, etc., is subjected to destructive distillation, the nitrogen of the nitrogenous compounds unites with hydrogen and escapes as ammonia gas. When bituminous coal, used in the manufacture of coal gas, is subjected to destructive distillation in iron retorts, the nitrogen of the coal escapes, combined as ammonia. The coal contains usually at least two per cent of nitrogen. In this process of manufacture the ammonia passes into cooled tubes and is taken up along with other substances by the water condensed at the same time. From this solution pure products are prepared. When this solution is treated with acids like hydrochloric acid, compounds are formed, which are obtained as solids when the

water is driven off. The compound with hydrogen chloride is called ammonium chloride, and is represented by the formula  $\text{NH}_4\text{Cl}$ . (See later on.)

For experimental purposes, ammonia is prepared from ammonium chloride by mixing it with slaked lime and heating the dry mass. It is also prepared by heating ammonium chloride and similar compounds with a concentrated solution of potassium hydroxide.

**Preparation.** — Take 10 g. of dry ammonium chloride and about 20 g. of slaked lime and mix them in a mortar. Place the mixture in a 100 cc. flask or large test-tube, and arrange for collection of gas by upward displacement. Collect in dry bottles. The bottles should be kept nearly closed while collecting, and if not used directly, should be placed on a glass or other smooth plate, on which is spread a little lard or oil, to completely close the mouths of the bottles. Collect a sufficient number of bottles of gas. Pass the gas for some time into 50 cc. of water, setting it aside for further examination. Notice the temperature of the water at the beginning and end of the experiment.

If the compound is prepared from ammonium chloride and potassium hydroxide, 10 g. of the chloride is used and 30 to 40 cc. of concentrated solution of potassium hydroxide (KOH). The same apparatus may be used as was employed in the first method. The mixture is gently heated, the amount of heat being regulated by the flow of gas. The gas should also be dried by passing it through a calcium chloride drying tube.

Mix a few pieces of gelatine with a little slaked lime or (better) soda-lime, and heat in a test-tube. Examine the product with litmus and by the sense of smell. What is one of the substances that escapes? Feathers, wool, hair, and similar compounds may be examined in the same way. All these substances contain nitrogen in relatively large amounts.

**Experimental Study, No. 26.** — (a) Moisten a piece of red litmus paper and place it against the bottom of a bottle filled with air. Invert it and place it over a bottle of ammonia gas. What two facts are shown by this experiment?

(b) Place the mouth of a bottle of the gas under water and remove the cover. Note and explain the result.

(c) Determine accurately the volume of the 50 cc. of water through which the gas was passed. Is it more or less than it was before? Weigh 20 cc. of the solution and compare it with the weight of the same volume of water.

(d) Take 10 cc. of the solution of the gas and boil it for a short time. Examine the escaping gas with nose and with litmus paper. If the water is saturated with gas under ordinary temperatures and pressure, it has taken about 7270 cc. of gas. Compare this volume with the new volume of the gas.

(e) Test the gas with a burning stick and with a bit of ignited phosphorus. Why is there no chemical action?

(f) Heat a platinum wire (or a piece of foil), wound in the form of a small spiral, until it is red hot. Now place this in the mouth of the reagent bottle containing concentrated ammonium hydroxide. Shake the bottle before removing the stopper for the insertion of the wire. What gases are in the mouth of the bottle? What gas is on the surface of the wire? (See page 28.) Why does the wire glow? What must be going on? Explain how one of the conditions necessary to chemical change is met here. What are the products of this chemical change?

(g) Pass the gas through a tube heated to redness, and ignite the escaping gas. Prove that water is formed. Try to ignite the escaping gas when it has not been heated. What is the difference?

(h) Fill a dry bottle with dry hydrogen chloride, and when it is completely full, place it mouth to mouth over the same sized bottle of ammonia gas. Compare the substance formed with that from which the ammonia gas was prepared. Notice

whether either gas is present after the action ceases. How can you tell? What are the products?

(i) Perform the same experiment with chlorine gas and ammonia gas. Examine the product with litmus. Place 10 cc. of water in the bottle in which the action took place. Shake well and test the water with a few drops of silver nitrate solution. What substance does this prove is formed?

(j) Take 20 cc. of the water solution of the gas, add a few drops methyl orange solution, and run in slowly, by means of a pipette or burette, a dilute solution of hydrogen chloride (10 per cent solution), until the neutral point is reached. Notice how many cubic centimetres of the acid solution is used. Repeat this with 20 cc. and 30 cc. of the gas solution, noting each time how many cubic centimetres of the acid solution is used. Next, place all the resulting solutions in an evaporating-dish and evaporate to dryness (a low temperature should be used after most of the water has been driven out). Compare the product with ammonium chloride used in preparing ammonia; *e.g.* heat separately in a test-tube a little of each solid with a solution of potassium hydroxide, and examine odor of escaping gas; also examine the gas with litmus. Treat a little of each substance with concentrated sulphuric acid and examine in the same way as in the preceding case. Dip a glass rod in a solution of silver nitrate, warm the test-tube, and place the rod in the mouth of the tube. Into what two compounds have you separated the residue? Can you say that they are identical; *i.e.* the ammonium chloride and the residue? How is a body identified?

**Physical Properties.** — This compound of hydrogen and nitrogen is a gas. It is colorless, has an alkaline taste, and a characteristic odor. It is a powerful irritant when inhaled, destroying even the membranes of the mouth, nose, and lungs. It is lighter than air, having a density of 8.5. It is quite readily converted into a liquid under a pressure of 7 to 8 atmospheres

at  $15^{\circ}$ . At  $-50^{\circ}$  it is a liquid at ordinary pressure. It is very soluble in water; that is, 1 vol. of water will absorb about 1000 vols. of gas under standard conditions, or 1 g. of water at  $0^{\circ}$  will absorb .785 g. of ammonia gas. At  $15^{\circ}$  and 760 mm. pressure, 1 vol. of water absorbs 780 vols. of gas. The whole of the gas escapes on boiling the solution. It escapes slowly at ordinary temperatures.

**Chemical Properties.** — Ammonia gas does not unite with the oxygen of the air; in other words, the oxygen of the air does not decompose ammonia gas at ordinary temperatures. Under the conditions that obtain when a red-hot platinum wire is placed in a mixture of air and ammonia gas or of pure oxygen and ammonia gas, the union does take place, and water is formed and nitrogen set free. Only those elements that have a great affinity for hydrogen decompose it; such elements, for example, as chlorine, when hydrogen chloride is formed and nitrogen set free. It unites with hydrogen chloride without decomposition, forming a compound called ammonium chloride ( $\text{NH}_4\text{Cl}$  or  $\text{NH}_3\cdot\text{HCl}$ ).

The water solution of ammonia is alkaline to litmus paper and neutralizes acids in a similar manner to sodium and potassium hydroxide; that is, the law of constant proportions is obeyed, and a neutral body is formed by the chemical action. The product in the case of hydrogen chloride is the same as that formed when the gases are brought together; namely, ammonium chloride.

*Formula for the Compound of Hydrogen and Nitrogen, and Atomic Mass of Nitrogen.*

It has been shown that the compound consists of hydrogen and nitrogen only, and that but one stable combination of these elements is known.

**Quantitative Composition.** — The ammonia can be analyzed

by taking a definite weight of the gas and decomposing it by means of oxygen, weighing the water thus formed, and from this weight determining the amount by mass of hydrogen; and since the compound consists of hydrogen and nitrogen only, the difference between the mass taken and its mass will give the amount of nitrogen. Its gravimetric composition may be determined by a study of its volumetric composition.

**Experimental Study, No. 27.** — One hundred cubic centimetres of the dry ammonia gas are collected in a eudiometer tube over mercury. Electric sparks are now passed until the volume of the gas remains constant. (There is left undecomposed about three per cent of ammonia.) This will require the passage of the spark for a long time. The first fact to be noticed is that the volume of the gas is doubled; that is, it has become 200 cc. under the same conditions. The next question is, How much of this gas is nitrogen and how much is hydrogen? Use is here made of the fact that hydrogen unites readily with oxygen at high temperatures, while nitrogen does not unite with it. The volume of the mixed gases being accurately known, oxygen is passed into the tube until (say) 100 cc. have been added; the exact volume, however, must be determined. An electric spark is passed, and from previous experience we know that the hydrogen unites with oxygen to form water. What is its volume now? The volume of the remaining gas is properly determined and is found to be 75 cc. Since 300 cc. of mixed gases were in the tube before the explosion, 225 cc. of gas have disappeared. This 225 cc. of gas must have been hydrogen and oxygen in the proportion of 2 vols. of hydrogen and 1 vol. of oxygen. Hence two-thirds of 225 cc. was hydrogen gas (or 150 cc.), and the remainder (75 cc.) was oxygen gas. Now of the 75 cc. of gas remaining, 25 cc. is oxygen and 50 cc. is nitrogen. The amount of oxygen gas may be determined by passing into the tube 10 to 15 cc. of potassium pyrogallate. (See page 70.) Therefore the 200 cc. of mixed gases con-

tained 150 cc. of hydrogen and 50 cc. of nitrogen, or there were three volumes of hydrogen to every volume of nitrogen.

Analyses made in several ways all show the same proportion, by volume, of the two elements. The following is a description of one of the methods commonly used to determine the quantitative composition of ammonia gas. A long tube (closed at one end) is provided with a stop-cock within about 10 cm. of the other end, thus leaving a short open tube. The tube is next filled with pure chlorine gas; the tube can be filled over mercury or over a saturated solution of sodium chloride. The stop-cock is closed and the tube is placed with the open end uppermost. The short tube is next filled with the concentrated solution of ammonia gas, or ammonium hydroxide. Next, open the stop-cock and allow the solution to drop slowly into the chlorine gas. Continue this as long as any reaction occurs. How is this determined?

Now fill the short tube one-half full again of the ammonium hydroxide solution and admit this to the long tube, being careful that no air enters. Fill the short tube with sulphuric acid and close it, by means of a rubber stopper through which passes a glass tube so bent and of such a length that the open end can be placed in a beaker containing more of the dilute sulphuric acid. Fill this tube completely with the acid solution or with water, being sure that there is no air at any point above the stop-cock. Next, immerse the long tube in cold water and slowly open the stop-cock, leaving it until the pressure is equalized. The apparatus is next brought to the same temperature that it had when it was filled with the chlorine gas. The remaining gas is what? Explain why the second amount of ammonium hydroxide was added, and why the sulphuric acid was used. The volume of the remaining gas is one-third of the volume of the chlorine. How does chlorine gas combine with hydrogen gas by volume and by mass? Therefore, how much hydrogen by volume was there, and how much by mass?

When the water solution of gas is acted upon by the electric current, it is decomposed instead of the water, the gases collecting the hydrogen at the negative pole, and the nitrogen at the positive pole. The apparatus is shown in Fig. 6, page 81.

The calculation, therefore, of the mass proportions is now easily made. One hundred and fifty cubic centimetres of hydrogen weigh how much? Fifty cubic centimetres of nitrogen weigh how much? One hundred cubic centimetres of ammonia weigh how much? Under standard conditions, or any known conditions, it is understood in each case. It will be found by this calculation that 17.65 per cent of the compound is hydrogen and 82.35 per cent is nitrogen.

The facts, therefore, for the determination of the formula for ammonia and the atomic mass of nitrogen are : —

(a) The compound consists of 17.65 per cent of hydrogen and 82.35 per cent of nitrogen.

(b) The density of the gas is 8.5.

(c) The compound consists of 3 vols. of hydrogen and 1 vol. of nitrogen.

(d) The volume of the product of the union of the two gases is one-half the sum of the volume of the mixed gases ; *i.e.* three volumes or molecules of hydrogen unite with one volume or molecule of nitrogen and form two volumes or molecules of ammonia gas. How many atoms of hydrogen are there?

(e) The amount of nitrogen is the smallest amount found in any molecule or in the molecular mass of any compound.

The density of the gas being 8.5, its molecular mass is 17. Of this molecular mass 17.65 per cent, or 3, is hydrogen and 82.35 per cent, or 14, is nitrogen. From fact (e) the atomic mass of nitrogen is 14. Also, there are two atoms to the molecule of nitrogen, since its density is 14. Taking three parts of hydrogen as three atoms, the formula for ammonia is  $\text{NH}_3$ . Again, considering fact (d), three volumes of hydrogen unite with one volume of nitrogen, or three molecules of hydrogen



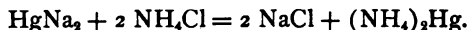
react with one molecule of nitrogen to form two molecules of ammonia. But three molecules of hydrogen contain six atoms ; therefore each molecule of ammonia gas contains three atoms of hydrogen, and since one molecule of nitrogen contains two atoms, the molecule of ammonia gas contains one atom of nitrogen.

**Reactions and Equations.** — Having obtained the formula for ammonia gas, the following reaction should be studied : —

(1) $N_2$	+ 3 $H_2$	= 2 $NH_3$	Read this by volume and mass.
(2) $NH_3$	+ $O_2$	= $N_2$ +	Complete and explain.
(3) $NH_3$	+ $Cl_2$	= $HCl$ + $N_2$	" " "
(4) $NH_3$	+ $Cl_2$	= $NH_4Cl$ + $N_2$	" " "
(5) $NH_3$	+ $H_2O$	= $NH_4OH$	" " "
(6) $HCl$	+ $NH_3$	= $NH_4Cl$	" " "
(7) $HCl$	+ $NHOH$	= $NH_4Cl$ +	" " "
	$HCl$ + $KOH$	= $KCl$ +	" " "
(8) $NH_4Cl$	+ $KOH$	= $KCl$ +	" " "
(9) $NH_4Cl$	+ $Ca(OH)_2$	= $CaCl_2$ +	" " "

**Ammonium Hydroxide and Ammonium.** — The solution of ammonia in water is variously named ; *e.g.* ammonia water, ammonium hydroxide, aqua ammonia, and the volatile alkali. As has been seen, this solution is alkaline to litmus, and neutralizes acids in a manner similar to potassium hydroxide. The gas also neutralizes acids, but differs from the action of potassium hydroxide in that no water is formed, the two molecules, ammonia and acid (*e.g.*  $HCl$ ), uniting to form one molecule. This is a peculiarity of most molecules containing nitrogen that act as bases. For reasons to be developed further on, it is supposed that a group of atoms,  $NH_4$ , called a radical, replaces one of the atoms of hydrogen in water, and accordingly the formula is written  $NH_4OH$ . Such a compound has never been separated from the water solution. That the group  $NH_4$  does exist is supported by the supposed formation of the so-called ammonium amalgam. This is made by treating sodium amalgam ( $HgNa_2$ )

with ammonium chloride ( $\text{NH}_4\text{Cl}$ ), which is shown by analysis to contain 14 parts of nitrogen, 4 parts of hydrogen, and 35.37 parts of chlorine. The following reaction is supposed to occur : —



In other words, the great affinity of the sodium for chlorine causes it to take the chlorine and thus leave the group  $\text{NH}_4$  free, when the latter unites with the mercury. Some recent observations seem to throw doubt on this explanation of the changes that occur.

**Name and History of Ammonia.** — The name of this compound according to the system of nomenclature should be *hydrogen nitride*, but the older name, given to it by Bergmann in 1782, is the one most commonly used. This name originated from the name *sal ammoniacum*, which was applied to a salt formed with ammonia and hydrogen chloride, from which the gas was obtained. This salt (ammonium chloride) received its name from the Egyptian temple Jupiter Ammon, near which the salt was made by distilling dung of camels. Ammonia was known to the early chemists at least as far back as Basil Valentine's time. It was, however, only known in its water solution. Priestley separated it from its water solution in 1784, and named it "alkaline air." Its composition was determined by Sir Humphry Davy and others, 1800–1809, by means of its decomposition by electricity.

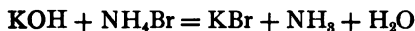
The water solution of ammonia was, and is sometimes now, designated as spirits of hartshorn, because it was prepared by the dry distillation of the hoofs and horns of animals.

**Uses and Tests.** — Ammonia and ammonium hydroxide are used in many ways. The gas is used extensively in making ice, in the preparation of the aniline colors, and of the carbonate of soda. The hydroxide is used as a laboratory reagent. It is also used as an antidote in overdoses of laughing-gas, chloro-

form, and ether. Its salts find extensive application in the arts and manufactures.

It can readily be detected, if free, by its odor and alkalinity and its action towards hydrogen chloride, unless it is present in very small quantities. It is then tested for by a special reagent, called Nessler's solution or reagent, which produces a brown coloration, in a water solution of the gas, when only a mere trace is present.

When in combination, it is set free by potassium or sodium hydroxide and then tested for in the manner just given.



*Compounds of Nitrogen with Members of the Chlorine Family.*

Nitrogen has been described as a substance chemically inert or nearly so. However, nitrogen under proper conditions does unite with each member of the chlorine family, especially with chlorine and iodine. These compounds are extremely unstable, the union being broken up and the elements set free by mechanical means or by a slight rise in the temperature. Contact with certain substances like oil of turpentine and caoutchouc causes the decomposition of the compound.

Nitrogen trichloride ( $\text{NCl}_3$ ), corresponding to ammonia, was discovered in 1811 by Dulong, who suffered the loss of three fingers and one eye during its investigation. The compounds with chlorine and bromine are heavy, oily appearing liquids, while those formed with iodine are solids. All these compounds are too dangerously explosive to be studied experimentally. Their correct formulæ have not been accurately determined.

**AIR, OR THE ATMOSPHERE.**

It has been already determined that the air contains oxygen and nitrogen. It also contains in varying quantities, although always relatively small quantities, several other substances, some of which are yet to be studied and will only be referred to here. Many other substances are present only in certain localities, as in large cities where the products of the burning of fuel and the destruction of many compounds send into the atmosphere their own peculiar products; *e.g.* hydrogen sulphide is produced when coal is burned, from decaying vegetation, etc. Ozone is also present at times in the air. The principal product of respiration and of burning of fuel—carbon dioxide—is always present. Besides the gaseous substances there are dust particles and living germs in all their various kinds, some of which are harmful, and some of which are beneficial, to life. Water is also present in the air in the form of vapor, in quantity varying with the nearness or remoteness of large bodies of water, mountain ranges, temperature, and pressure. The atmosphere rarely becomes saturated with water vapor; that is, in such a condition that it can hold no more, or if the conditions were changed by a slight fall of temperature, or even an increase of pressure, it would deposit water.

A litre of pure dry air weighs under standard conditions 1.2926 g., and therefore is 14.43 times as much as a litre of hydrogen.

There are three questions to be answered in reference to the air: (1) What are the amounts by volume and mass of each of its constituents? (2) Are the two chief constituents chemically combined? (3) Are the proportions of oxygen and nitrogen changing?

**Experimental Study, No. 28.** — (*a*) The removal of the oxygen in the air by means of phosphorus. Proceed with this

experiment, as was done in the preparation of nitrogen, except that the cubical contents of the gas-bottle must be known and care must be taken to prevent the escape of the air at the beginning of the experiment; also, the bottle must stand until the temperature within the bottle is the same as when the volume of the air was first measured.

(*b*) A more accurate result can be reached by using an accurately graduated eudiometer tube. Invert the tube over water or (better) over mercury; clamp it in position, equalizing the pressure inside and outside the tube. Determine and note the volume of air in the tube. Pass up into it a thin stick of phosphorus, the surface of which has been entirely freed from any oxide, and allow it to stand in contact with the air from twenty to thirty hours. Determine the volume of gas remaining under the original conditions. It is best to reduce both, volumes to volumes, under standard conditions. Examine the gas remaining. What is it? Determine from this experiment the mass of oxygen and nitrogen in the air, neglecting other constituents.

Many other ways have been used to determine the quantitative composition of the air; *e.g.* the absorption of the oxygen by potassium pyrogallate, or by passing the air over red-hot metallic copper, and by mixing with a known volume of air a known volume of hydrogen and causing the hydrogen and oxygen to unite by means of an electric spark. The method of procedure in the last process is very like that described for the determination of the hydrogen in the mixed gases formed from the decomposition of ammoniac. Fifty cubic centimetres of air are measured in a eudiometer tube, and 25 cc. of pure hydrogen is run into the tube, making 75 cc. of mixed gases. The spark is passed, and the volume of gas remaining will be found to be 43.575 cc., or there has been a loss of 51.425 cc. This loss represents the number of cubic centimetres of hydrogen and oxygen that have united to form water. But we know

that one-third of this volume (or 10.475 cc.) is oxygen. Therefore in 100 vols. of air there are 20.950 vols. of oxygen and 79.05 vols. of nitrogen. The weight of oxygen in 100 vols. can be determined by calculating the weight of 20.95 vols. taken as cubic centimetres or as litres, and thus the per cent by mass can be determined ; or the methods of Dumas and Boussingault can be employed.

The essentials of this latter process are : (a) the removal of the oxygen of the air by passing it over red-hot copper, when copper oxide ( $\text{CuO}$ ) is formed ; (b) the collection of the nitrogen ; (c) the weighing of copper oxide formed and calculating from this mass how much oxygen it contains, it being known that  $\frac{1}{8}$  of copper oxide is oxygen ; and (d) the weighing of the residual nitrogen. For a full description of the apparatus the reader is referred to larger works on chemistry. The result reached is the same as that found by the previous methods ; namely, that the air contains by mass 23.01 per cent of oxygen and 76.99 per cent of hydrogen.

**The Air not a Chemical Compound.** — At one time the air was regarded as a compound because its composition was constant (or nearly so) under all the conditions under which it had been examined. It is now considered merely a mixture, for the following reasons : —

1. All chemical compounds of nitrogen and oxygen contain these elements in the proportion of 14 parts by mass of nitrogen to 16 parts by mass of oxygen, or the proportions are simple multiples of these numbers. The proportion by mass of these two elements in air is 76.99 parts of nitrogen to 23.01 parts of oxygen.

2. If the air absorbed by the water is expelled and examined, it is found to consist of 29.7 parts of nitrogen to 16 parts of oxygen. These numbers, indicating the relative amount of the gases absorbed from the air by water, also indicate the actual amount absorbed from any known mixture of the two

gases. In other words, the law of absorption of gases by water is followed rather than the law of constant proportions, if taken in connection with the atomic masses of these elements as they are found in compounds.

3. The composition is not absolutely constant with reference to nitrogen and oxygen. The composition of air varies slightly, depending on the place from which the air is taken.

4. The air behaves chemically just as a mixture of the two gases in the proportions given behaves ; that is, its oxygen acts just as the oxygen in a similar mixture acts. There is no change in temperature when the mixture is made — a characteristic of all chemical change.

From these facts it is concluded that air is a mechanical mixture, and not a chemical compound.

**Some of the Uses of the Constituents of Air.** — The oxygen of the air is necessary to all animal respiration ; its union with carbon furnishes a large per cent of all of the artificial heat of the world ; takes part in the decay of many kinds of organic matter. The nitrogen serves a useful purpose as a diluent for the oxygen, as can be noticed in the rate of combustion taking place in pure oxygen and in the air. The ammonia of the air, although in small quantities, — 1 to 50 parts in a million parts of air, — furnishes a necessary element (nitrogen) to plants. The other constituents of the air, especially carbon dioxide, will be taken up when these substances are studied.

---

## PHOSPHORUS.

**Occurrence and Distribution.** — The chemical character of phosphorus prevents its free existence in nature. It is quite widely distributed in combination with a metal, usually calcium, and with oxygen, the compound being known chemically as

calcium phosphate. The principal minerals containing phosphorus are apatite, phosphorite, and coprolite. Phosphorite is found in North and South Carolina, and in many of the islands of the Caribbean Sea.

In soils of granitic origin the phosphate was originally disseminated through the granite, and usually in small quantities. On the decomposition of this rock to produce soil, the phosphate is set free unchanged. Such a soil therefore contains but little of the phosphate, and is thus quite quickly deprived of this element. Combined phosphorus is found in nearly all waters; that is, in the sea-water, in wells, and springs, but always in very small quantities.

Phosphorus in some combination is essential to animal and vegetable life. Consequently all soils to be productive must contain some of its compounds naturally, or it must be added to them. Most of the so-called fertilizers contain phosphorus in the form of a soluble compound. Starting with the soluble phosphate in a given soil, the cycle of changes is, in general, as follows: The rootlets of the plant take up the soluble phosphorus compound and by the agency of the other organs of the plant it becomes a part of the plant tissue. But by the selective power of the plant tissue, most of the phosphorus is used in forming the tissue in the seeds and fruits, so that the ripened wheat, oats, etc., become the storehouse of the phosphorus compounds. The soil is thus deprived of this necessary element, and in some way it must be returned to it if it is to continue its fertility. The exporting of wheat, for example, from many countries, is not only depriving those countries of their food supply, but is taking away an element essential to the growth of their further supply. The grain and fruit become the food of animals, who use the phosphorus compounds for making the hard tissue of the body, especially in making the bone tissue. Phosphorus is also found in the soft tissue of the body, as the brain and other parts of the nervous system.

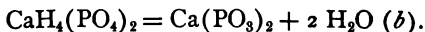


Some of the compounds of phosphorus leave the body in the excrement and in the urine. The bones are finally returned to the soil, are slowly disintegrated, and the phosphorus is again taken up by the plant, thus completing the cycle of changes.

**Methods of Preparation.** — Phosphorus may be prepared from any of its compounds found in nature, but is usually made from the bones of animals. After the 34 per cent of animal matter is removed from the bones by heat, the mineral matter which remains consists largely of an insoluble calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), from which the phosphorus is prepared by first treating with sulphuric acid, which causes the following reaction: —

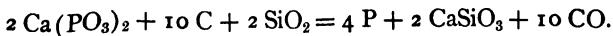


The calcium sulphate ( $\text{CaSO}_4$ ) is only slightly soluble in water, while the calcium tetrahydrogen phosphate is quite soluble. The mixture is treated with water, and the sulphate of calcium is filtered out, and the water in the remaining solution is evaporated away, leaving the solid residue containing the phosphorus compound. This residue is heated to redness, when the following reaction occurs: —



Compare the amount of oxygen in the calcium metaphosphate ( $\text{Ca}(\text{PO}_3)_2$ ) with the amount found in the original compound. Why did the oxygen leave the compound  $\text{CaH}_4(\text{PO}_4)_2$ ?

The metaphosphate is now mixed with the proper amount of charcoal and sand and placed in earthen retorts and heated to bright redness. The reaction is: —



Notice the cause of this change. Did any change occur at ordinary temperatures?

The phosphorus is set free in the form of a vapor which condenses to a liquid and finally to a solid in the cool parts of the apparatus. It is collected under water, and finally moulded into sticks, and in this form is sold in the market.

**Experimental Study, No. 29.** — (All experiments with phosphorus should be performed with great care. It should not be touched with the fingers unless it is wet, and when cut it should be either kept under water, or its temperature must be kept low by frequently dipping it in cold water.)

1. *An Examination of the Varieties of Phosphorus.* — Common variety.

(a) Note the color, structure, odor, and other physical properties.

(b) Take a piece about as large as a half-pea and place it in a test-tube containing 5 cc. of carbon disulphide; cork tightly and shake. Examine and set aside for future use. Does it dissolve? Does it dissolve in water? Is it a physical or a chemical solution?

(c) Examine a small piece of phosphorus in the dark after it has been slightly rubbed. Or dissolve a bit of it in olive oil by gentle heat, and shake, when cooled, in a tube containing air.

(d) Place a small piece of phosphorus in a tube or flask containing 50 cc. of water, and slowly warm, noticing the temperature at which the phosphorus melts.

2. *An Examination of the Red Variety of Phosphorus.* — Proceed in exactly the same way as in the examination of the common variety.

(e) Its chemical relation to the preceding element should be reviewed and recalled.

(f) Float two porcelain capsules in a large beaker or evaporating-dish which is partly filled with water. Place in one a bit of common phosphorus and in the other a little of the red variety of phosphorus. Slowly warm, and notice which inflames

first and the temperature of ignition ; that is, the temperature of the water in which the capsules float.

(g) Cover a small piece of each kind of phosphorus with iodine placed on the plate of the retort-stand. Leave in this position for several minutes, noting what occurs.

(h) Turn a portion of the solution of phosphorus and carbon disulphide on a piece of filter paper and place it on the base of the retort-stand and allow the liquid to evaporate. Explain what occurs. In what condition was the phosphorus?

(i) Add a portion of the carbon disulphide, or ether solution of phosphorus, to a water solution of copper sulphate ( $\text{CuSO}_4$ ). What is the deposit?

**Physical Properties.** — When the two kinds of phosphorus are compared physically, it is readily seen that they differ in structure, color, odor, and in fact in most of their physical properties.

The common variety of phosphorus is a yellow, waxy solid, having a crystalline structure, while the red variety is amorphous and is usually in the form of a red powder. The common variety is soluble in carbon disulphide, while the red variety is not. The specific gravity of the first is 1.83 and of the second 2.14.

If the yellow phosphorus is heated to  $240^\circ$  (to  $250^\circ$ ) away from oxygen, in any gas like nitrogen that has no action upon it, it is changed to the amorphous variety. If, however, the temperature is increased to  $260^\circ$ , it changes again to the yellow variety. When iodine is brought in contact with the yellow variety, a part of the phosphorus is changed to the red, and a part unites with the iodine. The red phosphorus is not phosphorescent and does not unite with oxygen as readily as the other varieties, it being kept with safety in the air. The yellow phosphorus melts at  $44^\circ$ , while the red variety requires a temperature of  $225^\circ$  before fusion takes place.

The vapor density of phosphorus, like that of sulphur, varies with the temperature to which it is subjected. At  $290^\circ$  it is

rapidly converted into a colorless vapor whose density is 61.92. This density remains quite constant, at least until a temperature of  $1040^{\circ}$  is reached. The density has been shown to decrease as the temperature rises above  $1040^{\circ}$ , and about 1440 is found to be 43.8.

The amorphous variety of phosphorus is prepared from the ordinary phosphorus by heating the latter in a close vessel for several days. The temperature is kept at  $240^{\circ}$ . The whole of the phosphorus is not changed, and the unchanged part is removed by solution in carbon disulphide.

**Chemical Properties.** — Chemically speaking, phosphorus is a very active element. The red variety is, however, much less active than the yellow kind. The yellow variety unites slowly with the oxygen of the air at ordinary temperatures, but the heat produced by the action soon raises the temperature sufficiently to cause rapid union. In pure oxygen gas it is said that it can be heated to a temperature of  $290^{\circ}$  without rapid oxidation, while in moist air it readily ignites at  $50^{\circ}$ . It may therefore be inferred that water has something to do with the action. The oxide of phosphorus that is formed is readily soluble in water. (See under PHOSPHORUS OXIDE.) It is found that phosphorescence is in some way connected with the presence of oxygen, for it does not possess this property in the presence of pure gases of other kinds, like hydrogen and nitrogen; but if a small quantity of oxygen is admitted to the tube containing phosphorus and hydrogen, for example, it regains this property. There are some gases and vapors that prevent its luminosity even if oxygen is present.

It unites with many other elements directly; for example, with chlorine, iodine, bromine, and sulphur. Its affinity for oxygen is so great that it decomposes many compounds containing it, especially salts of the metals, like copper, sulphur; the metal uniting with a portion of the phosphorus. Copper sulphate is decomposed, and copper phosphide ( $\text{Cu}_3\text{P}_2$ ) is

formed along with some copper phosphate. Silver nitrate ( $\text{AgNO}_3$ ) is decomposed, and silver phosphide ( $\text{Ag}_3\text{P}$ ) is formed. Silver nitrate is sometimes used in case of phosphorus burns to remove any free phosphorus.

In electrotyping, non-metallic objects are given the required conducting coat of metal by first dipping the objects in a solution of phosphorus in ether and then transferring them to a solution of copper sulphate, when a thin layer of copper is deposited on the surface.

The element is easily recognized by its chemical properties, and especially by its action with oxygen.

**Name and History.** — Phosphorus was discovered in 1769 by Brand, who prepared it from urine by evaporating the latter to dryness and mixing the residue with sand and igniting it. It was a rare and costly substance until Scheele showed in 1771 that it could be obtained from the ashes of bones. The name is derived from two words, *phos* (light) and *pherein* (to bear), referring to its light-giving properties.

**Uses and Manufacture.** — Phosphorus is used in manufacturing matches, in chemical laboratories, and in medicine. The amount required each year for these purposes is about 2600 tons. This is principally made at Birmingham, England, and at Lyons, France. Its manufacture is attended with much danger, especially because of its effects on the human body. It is an active poison when taken into the stomach, unless in very small doses, as is the case in phosphorus pills, which contain less than .01 grain or .6 milligrammes of phosphorus. In case the vapor is inhaled in small quantities for a long time, as may be done by workmen during its manufacture, it produces a disease of the bones called necrosis, which causes them, principally those of the jaw, to be decomposed. They are slowly removed from the body by ordinary processes of the system. The principal use of phosphorus is in match-making, which will be described under the study of potassium chlorate. Most

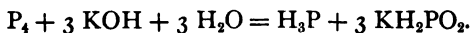
of the amount manufactured is used for this purpose. The red variety is now used for this purpose since it can be handled without danger to the workmen.

*Compound of Phosphorus and Hydrogen.*

**Methods of Preparation.** — Phosphorus and hydrogen do not unite by merely bringing the elements in contact with each other, even if they are subjected to high temperatures. When the hydrogen is nascent, the union does take place at a gentle heat. The hydrogen may be generated by the action of zinc and sulphuric acid. The amount of the compound produced in this way is small, and other methods are commonly used to prepare it.

We have seen that phosphorus unites with the metals forming compounds similar to those formed by sulphur and the metals. In the latter case it was found that the metals in the compounds readily exchange places with the hydrogen of the acids. For example, in the formation of hydrogen sulphide acids, like sulphuric acid, when acting on iron sulphide ( $\text{FeS}$ ), take the iron and supply its place with hydrogen. The metallic phosphides act in a similar manner. When calcium phosphide is treated with hydrogen chloride, the compound of phosphorus and hydrogen is produced, the calcium uniting with the chlorine of the acid.

The most convenient method of preparing this hydrogen compound of phosphorus is to heat the phosphorus with a concentrated solution of potassium hydroxide, when the following somewhat complex reaction takes place : —



**Preparation.** — A 250 to 300 cc. flask is about one-half filled with a concentrated solution of potassium hydroxide, and there are added several pieces of phosphorus about the size of a

pea. Next add 1 to 2 cc. of ether, and arrange the flask for heating as is usual on the retort-stand. Fit the stopper as for collecting gases over water, only the stopper should have but one hole, and the tube running to the trough should be a glass tube properly bent; or a rubber tube will answer if it is supplied with a glass tip. The stopper is placed tightly in the flask and the end of the delivery tube put under water. Heat is slowly applied to the flask, care being taken to keep the end of the tube under water while the lamp is under the flask, but it must be removed when the heat is removed, unless the gas escapes freely. The gas does not escape until the flask has been heated for some time. Collect some of the gas in small ounce bottles—a sufficient number for an examination of its physical properties. In order to prevent any possible explosion or the breaking of the flask when the heat is removed, boiling water is added to the vessel in which the collecting-tube ends, the hot water being drawn into the flask as it cools.

**Experimental Study, No. 30.**<sup>1</sup>—(a) Examine some of the gas for its physical properties.

(b) Examine the gas and its products as it escapes into the air. Collect some of the fumes as they escape; dissolve them in water and test the solution with litmus. Compare the product with that produced when phosphorus is oxidized in air.

(c) Explain the motion in the “rings” of fumes formed when the gas ignites in the air; also, the flash of light at the time of the formation of the “rings.” What are the products? Compare them with the product of oxidizing phosphorus.

(d) Mix equal volumes of the phosphide and hydrogen chloride or iodide. The action is similar to that of ammonia and hydrogen chloride; that is, there is a direct union of molecules of hydrogen iodide, etc., with the hydrogen phosphide. The formula of the compound is accordingly  $\text{PH}_4\text{I}$ .

---

<sup>1</sup> See foot-note on page 155.

(e) Pass the gas through a solution of some metallic salt like copper sulphate. What is the deposit?

(f) Its action towards members of the chlorine family is very energetic, so much so that experiments with these substances are quite dangerous. The chlorine unites with the phosphorus to form a trichloride of phosphorus. What becomes of the hydrogen?

(g) Place a definite amount of gas in a eudiometer-tube and pass electric sparks until it is decomposed. The poles should be gas carbon. Note the volume of gas. What is the gas? Where is the phosphorus?

(h) Heat a portion of the hydrogen phosphide in a tube with metallic copper. Determine what the products are.<sup>1</sup>

**Physical Properties.** — Hydrogen phosphide is a colorless gas, possessing a disagreeable and perfectly characteristic odor, often described like that escaping from decaying fish. It is only slightly soluble in water and may be changed to a liquid, and finally to a solid form, by the usual means. The liquid boils at  $-85^{\circ}$ . It has a vapor density of 16.98.

**Chemical Properties.** — Hydrogen phosphide is an unstable compound, the chemical properties of which are those of phosphorus, apparently increased in many cases by the fact of its gaseous condition. The pure gas inflames in the air at  $100^{\circ}$ . It is decomposed by all the members of the chlorine family with explosive violence. It removes metals from their salts, giving its hydrogen to the acid of the salt. It unites with the acids of the chlorine family, forming salt-like bodies called phosphorum compounds, corresponding to the ammonium compounds. It is poisonous even in small quantities. The electric spark decomposes it into solid red phosphorus and free hydrogen, the volume of the latter being one and one-half times

---

<sup>1</sup> Experiments with hydrogen phosphide should be performed with great care. It is not advisable for the inexperienced student to prepare the gas or to perform any of the experiments just indicated.



that of the original gas, or two volumes of gas yield three volumes of hydrogen.

The same facts are demonstrated when the gas is heated with metallic copper.

*Determination of the Formula for the Compound of Hydrogen and Phosphorus, and the Atomic Mass of Phosphorus.*

**Facts.** — (a) The quantitative composition is shown by (g) ; that is, that 2 l. of the gas yield 3 l. of hydrogen. What does a litre of the gas weigh? What is the volume of the hydrogen when a litre of the compound is decomposed? What is the mass and per cent of hydrogen?

(b) The compound contains nothing but hydrogen and phosphorus ; therefore from the previous facts, what is the per cent of phosphorus in the compound?

(c) The density of the gas is 16.98.

(d) This is the smallest amount of phosphorus found in any molecule. From these facts show that the formula for the compound is  $\text{PH}_3$ , and that the atomic mass of phosphorus is 30.98.

**The Number of Atoms in a Molecule of Phosphorus.** — The density of phosphorus is 61.92. How many atoms are there therefore in a molecule, the atomic mass being 30.98?

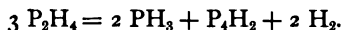
**Problems.** — How does the fact that two volumes of hydrogen phosphide yield three volumes of hydrogen tend to prove that there are three atoms of hydrogen in the molecule of phosphide?

If the molecule of phosphorus contains four atoms, how many litres of hydrogen will be required to unite with one litre of gaseous phosphorus?

**History and Name.** — Hydrogen phosphide ( $\text{PH}_3$ ) was discovered in 1783 by Gengembre, who prepared it by the process just described. Later on it was studied by Rose and found to



phosphide by exchanging one of its atoms of hydrogen for the group  $\text{PH}_2$ . Diphosphide of hydrogen decomposes readily into phosphide of hydrogen ( $\text{PH}_3$ ) and tetraphosphide of hydrogen ( $\text{P}_4\text{H}_2$  or  $\text{P}_2\text{H} = \text{P}_2\text{H}$ ).



The tetraphosphide of hydrogen is a solid readily decomposed, and is rapidly oxidized at a temperature of  $150^\circ$ .

In order to make the pure phosphide of hydrogen, calcium phosphide and hydrogen chloride or phosphonium iodide ( $\text{PH}_4\text{I}$  and  $\text{KOH}$ ) are brought together. The latter reaction is as follows : —



### *Compounds of Phosphorus with the Chlorine Family.*

In studying phosphorus its chemism for iodine was noted. Recalling the relative chemism of the chlorine group, it would be expected that all the other members of the group would form compounds with phosphorus. Compounds with each member of the group are well known; in fact, in case of chlorine and bromine two combinations are known. These compounds have a great theoretical and practical value. Their relative stability is in accord with the relative chemism of the halogens; that is, the fluorine compound is most stable, and the iodine compound is the least so. The pentafluoride of phosphorus is not dissociated even at high temperatures.

They may all be formed by the direct union of the elements which takes place with great energy; that is, with the development of a large amount of heat. The compound of fluorine is a gas having a density of 63 which corresponds to a compound having the formula  $\text{PF}_5$ . (How is this shown to be the correct

formula for the compound, the atomic mass of each element being known?)

With chlorine the direct union produces a compound which is a liquid boiling at  $76^{\circ}$ . Its vapor density is 68.535, corresponding to the formula  $\text{PCl}_3$ . Another compound with chlorine is known whose formula is  $\text{PCl}_5$ . This compound is a solid and is much used in the study of organic compounds containing hydroxyl, since it exchanges an atom of chlorine for this group, and thus affords a means of determining whether the hydroxyl group is present in the compound.

The compounds of phosphorus with bromine are produced by the direct union of the elements. The one corresponding to the formula  $\text{PBr}_3$  is a liquid which boils at  $175^{\circ}$  and has a vapor density of 135.1. The compound  $\text{PBr}_5$  is also known.

Iodine also forms compounds with phosphorus by the direct union of the element, especially when there is an excess of iodine present. The compound corresponding to the formula  $\text{PI}_3$  is a solid, crystallizing in six-sided crystals.

Each of these compounds decomposes water, forming the hydrogen compound of the halogen and an acid of phosphorus, to be studied later on.

---

### ARSENIC.

**Occurrence and Distribution.** — Arsenic, unlike phosphorus, occurs free in nature, in quite large masses, especially in Siberia. It, however, is widely distributed in combinations with sulphur, often in connection with sulphides of many of the metals, such as iron, nickel, and cobalt. These ores vary greatly in composition; sometimes, as in mispickel, arsenic, iron and sulphur are united; again, iron and arsenic, or nickel and arsenic, form an ore.

**Methods of Preparation.** — The natural arsenic is rarely quite free from other elements, but is sufficiently pure for most purposes. The commercial supply is, however, from the ore called mispickel, or arsenical pyrites. The process of preparation depends on the fact that heat decomposes the compound, and that the arsenic at the temperature of decomposition is a vapor. The ore is represented by the formula  $\text{Fe}_2\text{S}_2\text{As}$ . This compound becomes, on heating away from the air,  $2 \text{FeS} + \text{As}$ .

The arsenic is condensed in an appropriate tube and is further purified by mixing it with a little charcoal and distilling off the arsenic. The charcoal removes any oxygen that may be in combination with the arsenic. There is also found native the trioxide of arsenic, called arsenolite, which is mixed with charcoal and heated in closed retorts, when it is used as a source of arsenic. The carbon removes the oxygen, forming carbon dioxide, which is a gas, and the heat vaporizes the arsenic, which is condensed in the cool part of the apparatus.

**Experimental Study, No. 31.**<sup>1</sup>—(a) Place in an ignition-tube, or in special tubes called arsenic tubes, a small amount of the oxide of arsenic; next place on top of this powdered charcoal, filling about one inch of the tube. Heat the charcoal until it is red-hot, and while it is hot, heat the part of the tube containing the oxide. The deposit on the cool part of the tube is arsenic. Examine this. Use a magnifier. What becomes of the oxygen of the oxide? Why heat the charcoal first?

(b) Examine a specimen of arsenic for hardness, malleability, and solubility in water.

(c) Heat a bit as large as a pin's head in a test-tube and notice its odor.

(d) Determine lustre, brittleness, and crystalline character.

---

<sup>1</sup> All experiments with arsenic should be made with the distinct understanding that it and all its compounds are poisonous substances whether inhaled or swallowed.

(e) Prepare a tube about 10 cm. long and 5 mm. wide by closing one end. Place in this a piece of arsenic as large as a pea and close the other end of the tube. Heat the tube to a high temperature for some time and notice the changes that occur in form of the arsenic. When the tube is cool, break it and examine its contents.

(f) Heat a bit of arsenic in the air in a test-tube. About what is the temperature at which the change occurs?

(g) Sprinkle finely powdered arsenic in a bottle of dry chlorine or bromine gas. Place 10 cc. of water in the bottle; close and shake well. Test the solution with litmus paper. What is the white deposit? Filter out the deposit and test the solution with a few drops of silver nitrate, adding first a little nitric acid. Explain the result.

(h) Mix a little arsenic with twice its volume of sulphur. Does any change occur in the mixture? Place the mixture in a tube and heat it. Powder, and examine the residue for free arsenic. Note any changes that occur.

(i) Moisten a small amount of powdered arsenic and warm in an open dish to about  $100^{\circ}$  for some time. Replenish water as it escapes. What is the white or grayish powder? What has produced the change?

(j) Heat a little arsenic and powdered zinc together in an ignition-tube and note the results. What name should be applied to this compound?

**Physical Properties.** — Arsenic is a solid resembling in general appearance many of the metals. It has a steel-gray color and a metallic lustre. It is brittle, and the ordinary variety is crystalline. There is an amorphous variety formed by heating the ordinary kind in a stream of hydrogen. This latter variety is black and lustreless, and its specific gravity is 4.71, while the crystalline variety has a specific gravity of 5.7. At  $360^{\circ}$  the amorphous is changed to the crystalline form.

Arsenic is converted into a vapor apparently without passing

through the liquid state, but when heated in a closed tube it fuses. The density of arsenic vapor at red heat is 150. (Its density decreases as the temperature rises, and at 1437° it is 94.5.) Its molecular mass is therefore 300.

The odor of arsenic vapor is characteristic and resembles that of garlic.

**Chemical Properties.** — Arsenic is not a very active element at ordinary temperatures, chemically speaking. The oxygen of dry air does not attack it until heated to about red heat. In moist air it slowly oxidizes. It unites directly with the halogens and with most of the metals, and with many non-metals, at high temperatures. The *metal* arsenic is not poisonous when swallowed, probably owing to the fact that it is insoluble in the liquids of the stomach. Its soluble compounds are, however, very active poisons.

**History and Name.** — The name *arsenic* is derived from the word *arsenicon*, the Greek name for the native sulphide. The word signifies *potent* or *powerful*.

The alchemists were practically acquainted with arsenic, since they used it to change copper into a white metal, which they thought was one step toward the change of copper into silver. The metal was not known as such until 1694, when it was obtained by Schroeder. It was not well known until 1733, when Brandt made a careful study of it.

**Uses and Tests.** — Arsenic is used in making shot. It is found when molten lead is dropped in small quantities from a considerable height, that the drops assume a pear shape if cooled during the fall. But when arsenic is added to the molten lead, under the same conditions, the drops remain spherical. The lead also is hardened. About forty pounds of arsenic are added to each ton of lead. Compounds of arsenic are used in medicine, in the manufacture of fireworks, and as pigments in coloring. Arsenic is recognized by its physical properties and by the odor produced when it is heated in the air.

*Compound of Arsenic and Hydrogen.*

**Methods of Preparation.** — Arsenic does not directly unite with hydrogen; *e.g.* by heating it in an atmosphere of the gas. The methods for its preparation are analogous to those used for the preparation of phosphide of hydrogen; that is, the hydrogen must be in the nascent state, or it may be produced from a metallic arsenide by the action of an acid like hydrogen chloride. It is commonly prepared from the oxide of arsenic or from the arsenide of zinc. The compound is extremely poisonous, even if considerably diluted with air, and great care should be used in its preparation.

**Preparation.** — The nascent hydrogen is obtained from pure zinc and hydrogen chloride. The apparatus is fitted up in the same manner as is done for generating hydrogen, except that a piece of the glass tubing is drawn out to a fine jet and placed in the end of the connection-tube to be used as a jet for the oxidizing of the gas. The hydrogen is generated until it is safe to ignite it. A solution of the oxide of arsenic, or some soluble compound containing arsenic, is then added to the generator. The nascent hydrogen attacks the oxide and removes from it its oxygen, forming water; and the arsenic thus freed unites with more of the hydrogen. Several small bottles of gas may be collected.

**Experimental Study, No. 32.** — (*a*) Ignite the escaping gas and place in the flame a piece of cold porcelain (an evaporating-dish). Allow the porcelain to remain in the flame for an instant. Repeat this several times. What is the dark deposit? Compare it with the deposit on the side of the tube when arsenic was heated away from air. Why should it be formed? Explain thoroughly. Heat a piece of porcelain nearly red-hot and place it in the same flame and note the result. What are the white fumes?



(b) Heat the delivery tube a few centimetres from the jet and notice any changes in the flame. (The delivery tube may be wound in wire gauze to prevent its bending from the effects of the heat.) What is this deposit? What does this result say as to the stability of the compound?

(c) Remove the jet and put in its place a tube containing a little copper oxide, heating the tube where the oxide is and allowing the gas to pass over the red-hot oxide. Hold a cold beaker over the end of the tube from which the gas escapes. What does this result show? Arsenide of copper is formed in the tube.

(d) Metals like sodium or tin may take the place of the copper oxide, when hydrogen will be set free and the arsenide of the metal is formed.

(e) Collect some of the gas over water and notice its solubility.

(f) Treat the water solution with a few drops of chlorine water. Test the water with litmus. What is the deposit? Test the solution for hydrogen chloride. Explain the reaction.

(g) Leave some of the water solution exposed to the light and note the changes.

(h) Place a measured volume of the gas in a eudiometer tube and pass electric sparks until decomposition is complete. What is the deposit? What is the volume of the remaining gas, and what is it? Prove what it is.

(i) Pass the gas into a dilute solution of silver nitrate. Filter out the black precipitate and add hydrochloric acid to the filtrate as long as a precipitate is produced. What is this done for? Filter again and pass into the filtrate hydrogen sulphide, and compare with (i) of Experimental Study, No. 23. This precipitate is the sulphide of arsenic.

**Physical Properties.** — The arsenide of hydrogen is a colorless gas, having a characteristic garlic-like odor. It is soluble

in water, about five volumes of gas to every volume of water. Its density is 38.95. It is converted into a liquid under a pressure of one atmosphere and a temperature of  $-40^{\circ}$ .

**Chemical Properties.** — Hydrogen arsenide is quite stable at ordinary temperatures, but at high temperatures, about red heat, it is decomposed into arsenic, the amorphous variety, and hydrogen. It is decomposed by the oxygen of the air when ignited, producing water and oxide of arsenic. When the temperature is reduced by a cold body being placed in the flame, the arsenic is deposited in an elemental state. Hot copper oxide and hydrogen arsenide mutually decompose each other, copper arsenide and water being formed. The metals decompose hydrogen arsenide, forming the arsenide of the metal, and hydrogen is set free. The halogens set the arsenic free and form corresponding acids with the hydrogen. Even light will decompose the gas.

When hydrogen arsenide is passed into a solution of silver nitrate, the silver is set free along with other products. With salts of some of the other metals, like copper, an arsenide is formed under the same conditions. The electric spark will decompose the gas, setting the elements free, the volume of the hydrogen being one and one-half times the volume of the original gas. The same ratio of hydrogen is found when the gas is decomposed by tin or by potassium.

Unlike the analogous compounds of nitrogen and phosphorus, hydrogen arsenide does not form compounds with the halogen acids.

*Determination of the Formula of the Hydrogen Arsenide and the Atomic Mass of Arsenic.*

**Facts.** — (a) We have seen that when the gas is decomposed the arsenic is deposited as a solid and that the volume of

hydrogen is one and one-half times the original volume of the gas.<sup>1</sup>

The per cent of hydrogen is 3.85, and of arsenic it is 95.15.

(b) The vapor density is 38.95.

(c) One volume of arsenic vapor (?) unites with six volumes of hydrogen and forms four volumes of hydrogen arsenide.

(d) When the gas is decomposed, one volume forms one and one-half volumes of hydrogen.

(e) No molecule is known that contains a less portion of arsenic.

According to the reasoning previously given for the determination of formulæ of gaseous compounds, the formula of this compound is  $H_3As$ .

The vapor density of arsenic being 150 (at red heat), how many atoms are there in the molecule at this temperature? The molecule contains a less number of atoms at higher temperatures, since the density of the vapor decreases as the temperature rises.

**Name and History.** — Hydrogen arsenide was discovered by the Swedish chemist Scheele in 1755. The compound was formerly called *arseniuretted hydrogen*.

### *Arsenic and the Halogens.*

Arsenic unites readily with the halogens, forming with each a compound the molecule of which has the general formula  $AsX_3$ . They may be prepared by the direct union of the elements. They are all unstable compounds, being readily

---

<sup>1</sup> The student should calculate the per cent of hydrogen and arsenic in the compound, knowing the density of the gas to be 38.95, and taking into account the fact that the compound contains no other elements than hydrogen and arsenic. The arsenic may be also determined by heating the gas with copper oxide in the manner previously described and determining the arsenic in the arsenide of copper which was formed.

decomposed by water, even by the amount contained in the air, forming the corresponding hydrogen acid and the oxide of arsenic.

The vapor density of the compound of arsenic with fluorine is 65.95; that formed with chlorine is 90.5; that formed with bromine, 157.8; that formed with iodine, 227.3. The formulæ are therefore  $\text{AsF}_3$ ,  $\text{AsCl}_3$ ,  $\text{AsBr}_3$ , and  $\text{AsI}_3$ , respectively. Show how these formulæ are correct, the atomic masses of the elements being known, and the fact that one volume of arsenic unites with six volumes of each of the halogens, being also known.

## REACTIONS.

$\text{H}_2\text{SO}_4 + \text{Zn} + \text{As}_2\text{O}_3 = \text{H}_3\text{As} + \text{ZnSO}_4$	Balance, and explain reactions.
$\text{H}_3\text{As} + \text{O}_2 = \text{As}_2\text{O}_3 +$	Complete, and explain reaction.
$\text{H}_3\text{As} + \text{CuO} = \text{Cu}_2\text{As}_3$	" " " "
$\text{H}_3\text{As} + \text{Na} = \text{Na}_3\text{As} +$	" " " "
$\text{H}_3\text{As} + \text{Cl}_2 = ?$	" " " "
$\text{As}_4 + \text{H}_2 =$	" " " "
$\text{H}_3\text{As} + \text{e. current} =$	" " " "
$\text{CAsCl}_3 + \text{H}_2\text{O} = \text{As}_2\text{O}_3$	

## ANTIMONY.

**Occurrence and Distribution.**—Antimony occurs in nature in both the free and the combined state. Most of the antimony of commerce is obtained from the mineral sulphide of antimony, or gray antimony ore, sometimes called stibnite. It also occurs along with the sulphide ores of iron, copper, and lead. Stibnite is found principally in Hungary and in Cornwall.

**Method of Preparation.**—Antimony is prepared from its principal ore stibnite ( $\text{Sb}_2\text{S}_3$ ) by roasting, when both the sul-

phur and the antimony unite with the oxygen of the air. The compound with sulphur escapes as a gas, leaving the solid oxide of antimony. This oxide is treated in a closed vessel with charcoal, the carbon of which unites with the oxygen of the oxide, the antimony being set free.

It is also prepared by heating stibnite and iron together in a closed vessel until the ore fuses, when the sulphur unites with the iron, forming sulphide of iron ( $\text{FeS}$ ), leaving the antimony in the free condition.

**Experimental Study, No. 33.** — (a) Examine a piece of antimony for the usual physical properties; also for brittleness, by striking a piece with a hammer, the antimony resting on some hard surface. Examine structure. Place three or four grammes in a small iron spoon, cover with sodium carbonate, and heat to fusion. About what temperature does it fuse? What is the sodium carbonate for?

(b) Take a small bit of the antimony and heat it on charcoal with the blow-pipe. What do the white fumes indicate? They are the oxide of antimony ( $\text{Sb}_2\text{O}_3$ ). Note and describe this deposit.

(c) Heat a little of the sulphide of antimony in the same manner, noticing odor of any gases that escape. What are they?

(d) Heat in a small crucible a mixture of 2 g. of antimony sulphide with 1 g. of iron filings. The substances must be thoroughly ground together. The mixture should be well covered over with sodium carbonate and heated to a bright red heat for about fifteen minutes. Examine the contents and compare the solid with antimony. Where is the iron? What has become of the sulphur? Treat some of the solid material with sulphuric acid. What gas escapes? Explain its source.

(e) Place in a dry, tall gas bottle or jar a few drops of bromine, and when the bottle is filled with the vapor drop

in finely powdered antimony. (The taller the jar, the better.) Why? What is the evidence of chemical change?

(*f*) A bottle of chlorine gas may be treated with antimony in the same way as (*e*), noticing the same points.

(*g*) Heat, in a test-tube, powdered antimony thoroughly mixed with sulphur in a proportion of about two parts of antimony to one of sulphur. Remove the contents of the tube, powder, place a portion in a test-tube and add 10 cc. of hydrochloric acid. Warm. Explain result.

(*h*) Heat a little powdered antimony in a test-tube with concentrated hydrochloric acid. What gas escapes? Evaporate to dryness and examine the residue by treating a little of the solid residue with sulphuric acid and another portion with water. Note the results.

**Physical Properties.** — Antimony is a solid having the general appearance of a metal, and in fact partaking of the nature both of a metal and of a non-metal. It has a crystalline structure and is hard and quite brittle. Its color is silver-white, with a brilliant, metallic lustre. It fuses at  $425^{\circ}$  and is converted into a vapor at white heat. Its vapor density has not been definitely determined, but is said by Meyer to be 178.9. The molecular mass is therefore 357.8. It possesses the valuable property of measurable expansion when it solidifies from the liquid state.

**Chemical Properties.** — Antimony is not affected by the air at ordinary temperatures, but when heated it unites with the oxygen, forming an oxide of antimony ( $\text{Sb}_2\text{O}_3$ ). It readily unites with the halogens, the union being accompanied by light and heat. It unites with sulphur at a raised temperature, forming sulphide of antimony ( $\text{Sb}_2\text{S}_3$ ). It is dissolved in hot concentrated hydrochloric acid, hydrogen is set free, and a chloride of antimony is formed. It dissolves most readily in a mixture of hydrochloric and nitric acid; that is, in aqua regia.

**History and Name.**—The symbol for antimony (Sb) is derived from *stibium*, and this word is formed from *stibi*, the Greek name for the sulphide of the metal.

The word *antimony* is said to have originated from the fact that some monks of the middle ages were poisoned by using some of its compounds. The word, according to this derivation, is formed from *anti* (against) and *moine*, the French word for monk.

The element was first prepared by Basil Valentine in the fifteenth century.

**Uses.**—Antimony has few uses as a metal, but many of its compounds are used in medicine. It is also used, when it has been fused with lead and tin, for making type. The expansion of the antimony on solidifying permits the casting of the type, producing clearly cut characters. It renders the type metal of sufficient hardness to resist crushing and too rapid wearing out.

### *Compound of Antimony and Hydrogen.*

Antimony and hydrogen do not unite directly, but when the elements are in the nascent state they combine, forming a gaseous compound. The compound may be made by the action of nascent hydrogen (produced from sulphuric acid and zinc) on any of the soluble compounds of antimony. Or, it may be prepared by the action of sulphuric acid on an alloy of zinc and antimony.

**Preparation and Experimental Study, No. 34.**—Prepare a hydrogen generator with a jet at which the gas may be ignited in the manner described in the preparation of hydrogen arsenide. Dissolve a gramme or more of tartar emetic, potassium antimonyl tartrate ( $\text{SbOKC}_4\text{H}_4\text{O}_6$ ), in 20 cc. of water. Start the hydrogen generator, allowing the hydrogen to escape until it is safe to ignite it, when the solution of the antimony com-

pound is added through the thistle-tube. (Examination of the gas should be made under a good hood, or in a draught of air.)

(a) Ignite the gas and bring into the flame a cold porcelain dish or plate, removing it quickly. Make several such spots and examine and compare them with arsenic spots. Explain the formation of the spots. What is the white smoke formed by the burning? Hold a beaker over the flame. What does this result indicate? Put on one of the spots a few drops of a clear solution from bleaching-powder. Test an arsenic spot in the same manner.

(b) Pass the gas into a dilute solution of silver nitrate. Note the precipitate. Filter it out and wash it on the filter several times with water. When free from silver nitrate (how can this be determined?), wash the precipitate into an evaporating-dish and treat with hydrochloric acid and boil. Nearly neutralize the solution after it has been filtered (with ammonia hydroxide) and pass into it hydrogen sulphide ( $H_2S$ ). Note the color of the precipitate, comparing it with the precipitate produced by passing hydrogen sulphide into a solution of tartar emetic. (See (i) Experimental Study, No. 23.) The compound formed is a sulphide of antimony ( $Sb_2S_3$ ). Compare with the sulphide of arsenic, especially as to color.

(c) Collect some of the gas over water and examine it for its physical properties.

(d) Pass hydrogen sulphide into a bottle of the gas. What is the gas that remains? Examine it with a burning stick. What is the precipitate?

(e) Heat to red heat the tube through which the gas is escaping; while the jet is burning, note and explain any changes that occur in the color of the flame. What is the deposit?

(f) To a concentrated solution of sodium hydroxide in a test-tube add a few pieces of zinc and boil, noticing the evolution of hydrogen. Now add to the solution, while it is boiling,



a solution of a compound of antimony, and cover the top of the tube with a piece of filter paper moistened with a solution of silver nitrate. Is there any blackening of the paper? Compare with the result produced by passing the same gas into silver nitrate solution. Treat a compound containing arsenic in the same manner. Compare results.

(g) Treat a solution containing an arsenic compound in exactly the same way. What do these facts enable you to do?

**Physical Properties.** — Hydrogen antimonide is a colorless and odorless gas. It is only slightly soluble in water. It is a white crystalline solid at temperatures below  $-103^{\circ}$ , and is a gas at temperatures above  $-18^{\circ}$ . It is in part decomposed at this latter temperature. Its vapor density has not yet been determined. The best evidence, however, shows that it is 61.5.

**Chemical Properties.** — Hydrogen antimonide is an unstable compound, it being readily decomposed by heat and by sunlight. It burns in the air with a grayish blue flame, the products of the combustion being water and oxide of antimony ( $\text{Sb}_2\text{O}_3$ ). If the temperature of the flame be reduced by placing in it a cold body, the antimony is deposited unoxidized, producing the antimony spot. The antimony thus produced is insoluble in calcium hypochlorite, while a similar spot produced by arsenic is soluble. This serves as a means of distinguishing antimony from arsenic, as they may be found in their soluble compounds. When the hydrogen antimonide is passed into a solution of silver nitrate, a black precipitate is formed, which on analysis is found to consist of silver and antimony, to which the formula  $\text{Ag}_3\text{Sb}$  has been assigned. Hydrogen arsenide, under the same conditions, produces a black precipitate, which is, however, found to be pure silver. The arsenic is held in solution as arsenious acid, the compound having the formula  $\text{H}_3\text{AsO}_3$ . See under ARSENIUS ACID. Thus arsenic, which much resembles antimony, can be separated from it, and each element afterwards recognized by the usual tests.

Antimony can be distinguished from arsenic also by (f), called Fleitman's test. The hydrogen set free by the action of sodium hydroxide (NaOH) on zinc does not decompose antimony compounds, while it does react with arsenic compounds. The silver nitrate paper, therefore, will remain unchanged if antimony alone is present in the solution.

Hydrogen sulphide decomposes the gas, setting hydrogen free and forming sulphide of antimony. The same reaction occurs with hydrogen arsenide and hydrogen sulphide.

*Formula for Hydrogen Antimonide and Atomic Mass of Antimony.*

The compound is so unstable that it has not been studied as thoroughly as have been the other compounds of hydrogen and the non-metallic elements. Reasoning from its analogy to arsenic and from the formulæ of some of its other compounds, especially its compound with chlorine (which see), the formula for its hydrogen compound is determined to be  $H_3Sb$ . The atomic mass of antimony is 120.

*Compounds of Antimony with the Halogens.*

Antimony unites directly with the halogens, giving out heat and light. The compounds are solids at ordinary temperatures, but can be converted into vapor by heat. The compound with chlorine was prepared by the early chemists, and was by them called butter of antimony, a name which still clings to it. The name was originally applied to a distillate obtained by heating together corrosive sublimate and an ore containing antimony. The distillate resembled nearly colorless butter as it solidified on cooling.

The gas densities of these halogen compounds, in connection

with the facts of quantitative analysis, show that they should be represented by the formulæ  $\text{SbCl}_3$ ,  $\text{SbBr}_3$ ,  $\text{SbI}_3$ .

When the trichloride of antimony ( $\text{SbCl}_3$ ) is fused and subjected to the action of free chlorine for some time, a new compound is formed, which is a liquid, and to which the formula  $\text{SbCl}_5$  has been assigned.

Antimony also forms compounds with sulphur, as has been already seen. Two such compounds are known, represented by the formulæ  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ .

#### REACTIONS PRODUCED IN STUDYING ANTIMONY.

$\text{KSbOC}_4\text{H}_4\text{O}_6 + \text{H}_2 + \text{H}_2\text{SO}_4 = \text{H}_2\text{C}_4\text{H}_4\text{O}_6 + \text{SbH}_3 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$ . Balance.

$\text{SbH}_3 + \text{O}_2 = \text{Sb}_2\text{O}_3 + \text{H}_2\text{O}$  Balance and explain.

$\text{SbH}_3 + \text{O}_2 = \text{Sb} + \text{H}_2\text{O}$  " " "

$\text{SbH}_3 + \text{AgNO}_3 = \text{SbAg}_3 + \text{HNO}_3$  " " "

$\text{SbH}_3 + \text{HCl} = \text{SbCl}_3 +$  " " "

$\text{SbCl}_3 + \text{H}_2\text{S} = \text{Sb}_2\text{S}_3 +$  " " "

$\text{SbH}_3 + \text{H}_2\text{S} = \text{Sb}_2\text{S}_3 +$  " " "

$\text{SbH}_3 + \text{Heat} = \text{Sb} +$  " " "

$\text{Sb}_2\text{S}_3 + \text{O}_2 = \text{SO}_2 + \text{Sb}_2\text{O}_3$  " " "

Each of these equations should be read by mass and by volume when the product is gaseous.

#### CARBON.

**Occurrence and Distribution.** — Carbon exists in nature both as free carbon and in combination with other elements. As free carbon it is found in the crystalline condition, as in the diamond, and in the amorphous condition (usually) called graphite or plumbago. The diamond is not widely distributed, it being found in a comparatively few localities, the principal ones being in South Africa, Brazil, and India. Graphite is

found in masses in Siberia, in Europe, and in the United States. The principal localities in the United States are in California, New York, and Massachusetts. It occurs in small quantities widely distributed.

In various combinations with hydrogen, oxygen, and nitrogen, carbon forms an essential part of all animal and vegetable substances. Combined with hydrogen it constitutes the complex substance called petroleum, the source of a large number of the compounds studied under the subject of organic chemistry. Combined with oxygen and the metals it constitutes the compounds called the carbonates, such as limestone, marble, copper carbonate, etc.

It occurs in large quantities as mineral coal, which is the probable result of the decomposition of organic matter under certain natural conditions. Coal is not pure carbon, but contains besides this element substances that make up the ash of coal, hydrogen, oxygen, and nitrogen, and usually sulphur.

Charcoal is still another variety of carbon formed from vegetable matter by submitting it to destructive distillation.

**Experimental Study, No. 35.** — Carbon exists in three forms, represented by the diamond, graphite, and charcoal. These three forms can be best studied by comparing each with the others.

(a) Compare a specimen of diamond with one each of charcoal and graphite. (Specimens of black diamond can be obtained quite cheaply.) Rub each variety along a smooth and fairly hard surface. Rub the powdered graphite and charcoal between the fingers. Notice color, transparency, and hardness. Examine each kind with a microscope to determine structure, especially the structure of charcoal.

(b) Place a specimen of each variety in water. Force the charcoal into warm water in a beaker. Heat a piece of charcoal for some time in a covered crucible, and when cool place it in water. Explain the behavior of the different varieties under these conditions.

(c) Fill a test-tube with dry ammonia gas over mercury, and slip into the tube a piece of recently ignited charcoal, keeping the mouth of the tube under mercury. Compare this action with that of platinum towards such gases as oxygen, hydrogen, etc. In what condition is the gas after it is absorbed? Compare its volume with the original volume. Charcoal absorbs ninety times its own volume of ammonia.

(d) Place in a bottle 20 cc. of a water solution of hydrogen sulphide, and add a large spoonful of powdered charcoal. (Animal charcoal is best.) Close the bottle and shake it vigorously. Note the odor of the solution before and after this treatment. Where is the gas now? Allow it to stand for some time. Remove some of the charcoal and warm it. Does the hydrogen sulphide escape? What gas was present in the pores of the charcoal before it was put into the solution of hydrogen sulphide? How does it act chemically towards hydrogen sulphide?

(e) Place in each of three funnels on filter paper sufficient boneblack to nearly fill them. Pour into one of them a dilute solution of sulphate of quinine, and into another a solution of dark brown sugar, and into the third a dilute solution of cochineal. Examine the liquid as it comes through the filter. Return it to the filter and allow it to pass through a second time. Taste of the sulphate of quinine solution before and after filtering it. Note the effects in each case.

(f) Mix thoroughly  $2\frac{1}{2}$  g. of copper oxide ( $\text{CuO}$ ) with  $\frac{1}{4}$  g. of carbon. Place the mixture in an ignition-tube and heat to the temperature of the lamp. Examine the residue. What is it? Where is the carbon? What has the copper lost?

(g) Heat in a large test-tube fine pine shavings, and collect the gas given off over water. Reject the first bottle of gas. Test the gas with a burning stick. Examine the residue in the test-tube and compare it with charcoal. Heat a piece of each on a platinum foil. From whence was the gas? Ignite

the escaping gas at the jet, and while it is burning place in the flame a cold porcelain dish. What are the deposits?

(h) Heat some powdered graphite on platinum foil for several minutes. Does it oxidize?

(i) Mix a little graphite with potassium chlorate, thoroughly incorporating it by rubbing them together in a mortar, and heat for some time on the platinum foil. What element has been obtained from potassium chlorate? Recall the experiment of carbon and oxygen.

(j) Fasten a small piece of diamond on the end of a clay pipe-stem by means of plaster of Paris. Heat the diamond in an oxyhydrogen flame.

**Physical and Chemical Properties (a) of the Diamond.**—Physically speaking, the diamond is characterized by its hardness and peculiarities of crystalline structure. It is the hardest known substance, it being placed 10 in the scale of hardness of minerals. It is usually colorless, but is found in almost all colors to pure black. The crystalline faces of the diamond reflect and refract light, giving it a brilliant lustre. Owing to its highly refractive power much of the light that enters the diamond undergoes total reflection, and the art of cutting the diamond consists, in part, of so arranging these faces as to more perfectly produce the total reflection of light. The art of the lapidarist, by increasing the number of faces or facets, and by polishing them, has made the cut diamond the most brilliant and attractive of all the precious stones. The diamond can only be cut by using its own dust as the cutting instrument.

When heated, the diamond undergoes no change unless the temperature is very high, and then if shut off from air or from oxygen, it swells up into a black graphitic mass. At the temperature of the oxyhydrogen flame in pure oxygen it unites slowly with it, but at the temperature of the electric arc it unites rapidly with oxygen. At ordinary temperatures it is not acted upon by any chemical agent.

The diamond is practically pure carbon crystallized under conditions that have not been imitated in the laboratory. It occurs in crystals of several forms, but principally as octohedra and dodecahedra. These crystals are relatively quite small, the largest one known,<sup>1</sup> at present, weighs 72.5 g., or about  $2\frac{1}{2}$  oz., avoirdupois: this is owned by one of the Rajahs of Borneo. The cutting of the diamond usually greatly reduces its weight. The celebrated Kohinoor is said to have weighed over 3000 grains, but when it was brought to England from India it weighed about 590 grains, and by cutting it, it has been since reduced in mass to 338 grains. It now forms one of the jewels in the British crown.

Besides their uses for jewelry, diamonds are now used for drilling rocks and for cutting hard, brittle substances like glass. The scratch of the diamond determines the line along which the glass will break.

(b) **Graphite.**—When graphite is compared with the diamond or with charcoal, it has no apparent resemblances. Graphite, when powdered, is soft and greasy to the touch, but the individual particles are apparently very hard, as the tools used in cutting it are soon dulled. When rubbed on a surface, it leaves a black mark. This is true of lead or plumbum, and for a long time this substance was supposed to contain lead, hence the name plumbago, which is sometimes applied to it. The graphite has a specific gravity less than the diamond, it being generally 2.5 to 3.5 of the latter. Its color is grayish black, and its lustre is metallic.

When graphite is heated away from the air, the highest temperatures do not appear to affect it. If, however, it is heated in air or pure oxygen, or with some substance that readily yields oxygen, like potassium chlorate or lead chromate, it unites with the oxygen, forming the gas carbon dioxide.

---

<sup>1</sup> H. Emanuel, "Diamonds and Precious Stones."

Another peculiarity of this substance is its power to conduct electricity, while the diamond and charcoal are among the poorest conductors. The non-metallic elements, generally, are poor conductors of electricity.

It can be produced artificially, as in the making of cast iron, from 2 to 5 per cent of which is carbon. The carbon from which the graphite is formed is supplied by the fuel used for smelting the ore. The graphite is mixed with the cast iron and is set free when the iron is treated with hydrochloric acid.

The properties of graphite have made it useful for preparing pencils, for crucibles, when it is mixed with a little fire clay, as a packing for bearings to machinery, for polishing shot, gunpowder, iron stoves, and as a conductor for electricity.

(c) **Amorphous Carbon.**—There are several modifications of amorphous carbon; namely, charcoal, lampblack, coke, gas carbon, and animal charcoal. Some of these varieties are made distinct because of their source.

Charcoal is produced by heating wood to a high temperature away from the air. The various compounds that make up the wood are broken up into gaseous substances, carbon (charcoal), and mineral substances which constitute the ash of the burned charcoal. The pure charcoal can be made by heating some organic substance that contains no mineral matter, like starch or sugar, in a closed vessel to a sufficiently high temperature to decompose them. In this case the carbon is absolutely free from other matter. Wood, when thoroughly dried, contains about 45 per cent of carbon along with oxygen, and hydrogen, nitrogen, and the ash. A portion of the carbon escapes in combination with hydrogen, or with hydrogen and oxygen, forming a variety of compounds, such as acetic acid ( $C_2H_4O_2$ ), and methyl alcohol ( $CH_3OH$ ), creosote, etc., but a large part of the carbon remains behind. Water is also formed. Here again we have another illustration of the fact that different levels of temperature determine the chemical condition of the



elements. If we reduce the temperature low enough, many ordinarily unstable compounds are rendered almost perfectly stable; if the temperature to which compounds are subjected be sufficiently high (and that nearly always a possible temperature), most of the elements exist uncombined. Further, if at a certain degree of temperature certain elements remain in combination in a given proportion, at another degree of temperature different proportions are often in combination. The chlorides of phosphorus ( $\text{PCl}_3$  and  $\text{PCl}_5$ ) are examples. Wood, as used in the experiment, is principally cellulose, the molecule of which is represented by the formula  $\text{C}_6\text{H}_{10}\text{O}_5$ , or  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , but at  $1000^\circ$  these same elements are combined (or are free) in entirely different proportions.

When studying hydrogen it was noticed that platinum and other metals had the property of condensing gases on their surfaces. It may be stated as a general fact, that all solid bodies possess this property, but in varying degrees, the amount depending on the temperature of the solid, the surface exposed, and the nature of the substance. Carbon possesses this property to a marked extent. An examination of the charcoal shows that it is porous. (Why should it be porous?) The porosity of charcoal greatly increases its surface that may be exposed to gases, and consequently increases its absorptive power. Different kinds of wood when charred produce charcoals of different absorptive powers. Charcoal from cocoanut wood will absorb 171.7 vols. of ammonia gas and 17.9 vols. of oxygen gas under standard conditions, while the charcoal from ordinary wood will absorb less than half as much. The more compact the wood from which the charcoal is made, the greater is its absorptive power. The same facts, in general, are true of charcoal that are true of the platinum sponge; that is, if two gases are absorbed by the charcoal at the same time, and there is chemism between them, the chemical change takes place. Hence many of the noxious and odorous gases are

destroyed by being absorbed by the charcoal; *e.g.* hydrogen sulphide mixed with the air. In pure oxygen, the heat of the action, in many cases, is frequently sufficient to ignite the charcoal. If the products in any case are gaseous, they will obey the law of diffusion, and other portions of the original gases are absorbed, and the change is more or less continuous.

Charcoal also has the property of removing many soluble coloring-matters and many other soluble substances from their solutions. This property is possessed in a high degree by animal charcoal, so-called. Sugar solutions are rendered free from coloring-matter by filtering through layers of this charcoal; many of the alkaloids are absorbed, such as quinine and strychnine. Fusel oil is taken from alcohol by a similar process. In many cases the charcoal becomes inactive, but can be restored to activity by sufficient heating.

Pure charcoal carbon is odorless and tasteless, and is but little heavier than water, having a specific gravity of 1.57. It is infusible, non-volatile, and insoluble in any known liquid. Despretz is said to have volatilized a little carbon at the temperature produced by an electric current from 600 cells of a Bunsen battery. The carbon formed a crystalline deposit in the sides of the exhausted receiver in which the carbon poles of the battery were enclosed. He described the carbon as forming a black cloud in the receiver.

**Chemical Properties.** — Chemically speaking, charcoal carbon is practically inert at ordinary temperatures. Advantage is taken of this fact when posts are charred before placing them in the ground. Charred piles driven nearly 2000 years ago by the Britons, when removed were found almost completely preserved. Ink which was produced from lampblack has been found with Egyptian mummies unchanged. At the higher temperatures it possesses a marked chemism for many of the elements. It unites with oxygen, with sulphur, and with hydrogen. It will readily remove the oxygen from oxides of most

of the elements, and is therefore one of the principal substances used in preparing many of the metals from their compounds as they are found in nature. For example, such as iron ores, which are mostly oxides of iron.

**Animal Charcoal.** — Animal charcoal, as its name indicates, differs from ordinary charcoal in reference to its source, and consequently to a certain extent with reference to its composition. It is made by charring the bones and other animal substances out of contact with the air. It is more porous, — the carbon is more finely divided than it is in ordinary charcoal, — and it usually contains some nitrogen.

Coke, gas carbon, and lampblack or soot are the other varieties of amorphous carbon. They are all more or less pure carbon, formed under different conditions and from different materials. Coke is prepared from bituminous coal; gas carbon is formed by the decomposition of certain compounds of carbon and hydrogen at high temperatures, such as is found in the retorts in which ordinary illuminating-gas is prepared; lampblack or soot is formed when a body rich in carbon is burned in a small supply of oxygen, or when the temperature of the flame produced by such burning is in part reduced below the temperature of the ignition of carbon. Usually substances containing carbon and hydrogen and a small amount of oxygen, if any, are used in preparing the latter, such as petroleum, camphor, turpentine, tar, etc. The hydrogen of the compound unites with the oxygen of the air at a lower temperature than does the carbon, also more readily; and if only a small supply of oxygen is afforded, the carbon is deposited. Soot is quite pure carbon, the impurities being some of the undecomposed substances from which it is made.

The principal uses for lampblack are in printer's ink, India ink, as a black pigment, and for shoeblacking. Its use depends on its color and its indestructibility. Gas carbon is used in several forms of galvanic batteries.

**The Allotropic Forms of Carbon.** — If the allotropic forms of the preceding elements are compared with those of carbon, it will be noticed that those of the other elements tend to revert to a common form; *i.e.* to the form that exists under ordinary conditions. Also, that the various forms are readily produced from the common form, while the forms of carbon are perfectly stable, and one form is as permanent as the other; also, that they are not readily, or not at all, produced one from the other. They, however, all produce the same compound with oxygen, and also exactly the same quantity of this compound if the same mass of any pure variety is used.

Since carbon has not been converted into a liquid or into a vapor, no study of its properties in these conditions can be made. But if the conception that matter is made up of molecules, and that these molecules are in turn composed of a definite number of atoms,—and further, since these atoms and molecules can only differ in the arrangement of the atoms in the molecules, or in the arrangement of the molecules among themselves,—it may be inferred that these allotropic differences are due to the different arrangement of the molecules in the mass, or to a difference in the arrangement of the atoms in the molecule.

**History and Uses.** — Historically speaking, carbon has been known from the earliest times. The relations of the different varieties of the carbon to each other, however, was not known. The fact that a diamond was pure carbon, or that graphite was the same substance as charcoal, was not known until a comparatively recent time. At the suggestion of Newton, an Italian chemist heated a diamond in the focus of a lens, which caused it to entirely disappear. This was about the year 1700. It was not, however, until Lavoisier's time that the diamond and also graphite were definitely shown to consist of carbon.

The name *carbon* is derived from *carbo*, which means "charcoal." The symbol for the element is C. The rarity of

the diamond makes it the most valuable substance known to man. The Kohinoor diamond, which is in the crown of England, is valued at half a million dollars. The ancients ascribed to the diamond miraculous properties. It was thought to be able to control disease, to give to men the power of endurance, to make them brave and good. It was said to protect the possessor against lightning and against misfortunes.

The use of carbon as a fuel — in fact, as the great source of energy for mechanical purposes — has already been referred to. Again, as graphite in crucibles, it is used where a substance is required to withstand the action of great heat. Other uses of the different varieties of carbon have been pointed out in the preceding paragraph.

### *Compounds of Carbon with Hydrogen-Methane.*

**Occurrence and Distribution.** — The simplest compound of carbon with hydrogen, called methane, is found free in nature. It occurs where organic matter decomposes under water, and in general wherever such matter is decomposed away from oxygen. It is found in coal mines, and is there known as fire-damp. Its origin is undoubtedly connected with that of coal. It constitutes a large per cent of the so-called natural gas. Methane may be procured in warm weather from standing water in which there is organic matter, by stirring the mud at the bottom of the pool and collecting the gas as it rises. This gas is known as marsh gas, and contains about 75 per cent of methane. Methane is only one of a large number of compounds of carbon and hydrogen; but these compounds with others containing carbon are commonly studied under organic chemistry.

**Methods of Preparation.** — Carbon and hydrogen can be made to unite directly by means of electricity; the compound resulting is not methane, however, but is one of the other compounds of carbon and hydrogen called acetylene ( $C_2H_2$ ).

When very hot carbon (red to white heat) is brought in contact with water, the water is decomposed, and both its elements unite with the carbon, methane being one of the products. This is best done by passing steam over red-hot carbon contained in a porcelain or in any other infusible tube. The product is a mixture of the oxide of carbon, free hydrogen, and methane.

It is commonly prepared by treating sodium acetate with soda lime, which is a mixture of sodium and calcium hydroxides.

Methane may be prepared synthetically by heating together hydrogen sulphide, carbon disulphide, and copper. The copper has great affinity for the sulphur, thus setting the hydrogen and carbon free, which unite to form methane. The two compounds used here may be prepared from the elements, and thus the compound methane may be said to be formed synthetically from the elements.

**Preparation.** — Mix intimately 10 g. of *dry* sodium acetate with 40 g. of soda lime, or with 5 g. of powdered sodium hydroxide, and heat in a hard glass tube, or in an iron retort. Collect the gas over water. The gas may be made in large quantities and collected in an ordinary gas-holder, and if allowed to stand for a few days, impurities will be absorbed by the water.

To prepare methane synthetically, pass dry hydrogen sulphide with the vapor of carbon disulphide over copper which is heated to a red heat in a hard glass tube. The gas may be collected as before.

**Experimental Study, No. 36.** — (*a*) Place a bottle of the gas over a bottle of dry air; invert the bottles and allow them to remain in that position for a few minutes, then test the upper bottle of gas with a burning stick. (See *d*.)

(*b*) Shake a bottle of the gas with 20 cc. of water and note its solubility.

(c) Examine for and note other physical properties.

(d) Bring a burning stick to the mouth of the bottle of the gas. (The bottle is held mouth downward.) Push the burning stick up into the gas. Explain the result.

(e) Mix 1 vol. of the methane with 8 vols. of air; wrap a towel around the bottle and bring a burning stick to its mouth. Mix twice as much air by volume with the gas; *i.e.* 16 vols. of air and one of methane. Examine as before. Explain the different result.

(f) Fill a bottle over water or, better, over mercury one-third full of methane, and then completely fill with chlorine. Mix the gases thoroughly and bring a burning stick to the mouth of the bottle. Test the products with litmus. Add 20 cc. of water to the bottle; cover tightly and shake. Now acidify with nitric acid and then add a few drops of silver nitrate. What acid does the result indicate is present? What is the black deposit? The bottle should be kept covered with a towel to keep out sunlight. Explain the action.

(g) Fill a gas bottle with equal volumes of chlorine and methane. Cover tightly and leave the bottle in the sunlight. Note any changes in the color of the gases; after the changes are complete open the bottle and test the contents with litmus. Test the water solution as in (f) and answer the same questions.

(h) Light the gas as it escapes from the jet of the generating-apparatus, and hold over the flame a cold beaker glass. What is the liquid formed on the side of the glass? Explain the change.

(i) Place the burning jet in a bottle of air or, better, in a bottle of pure oxygen, keeping the bottle covered as closely as possible. When the action ceases, pour into the bottle a little lime water and shake. Notice the turbidity produced. Test the original gas in the same way. (This is a test for carbon dioxide ( $\text{CO}_2$ ), for which see page 301.) This result in con-

nection with (*h*) proves what, as to the elements in the compound?

(*j*) Collect over mercury in a eudiometer tube the methane, and note the volume. Pass electric sparks through the gas until its volume becomes constant. (The tube should be less than half full of methane.) Examine the gas remaining and the deposit on the platinum poles. What are they? What is the relative volume of the remaining gas?

**Physical Properties.** — Methane is a colorless, tasteless, and odorless gas. It is lighter than air, and next to hydrogen, the lightest known gas. Its vapor density is 8. It is slightly soluble in water and has been converted into a liquid by pressure and a reduction of temperature.

**Chemical Properties.** — Methane unites with oxygen to form water and carbon dioxide, the mixture of the two being explosive. A mixture of 1 vol. of air with 10 vols. of methane explodes most readily and powerfully. Less than 6 and more than 14 vols. of air to 1 vol. of methane do not explode, but they quietly unite. It is the mixture of methane and the air in the right proportions that causes the explosions that sometimes occur in coal mines. The gas has been formed during the time of the changes of vegetable matter into coal, and is held in the cracks and in the cavities of the coal deposit. When these are opened by the miner's pick, the gas escapes into the mine, and consequently becomes mixed with the air, often in quantities sufficient to produce explosive mixtures unless removed by proper ventilation. The heat of the miner's lamp is sufficient to ignite the gases. The products of this union are deadly in their effects, and are fatal to the miner if the explosion itself has not already proved so. The explosions are much less frequent at present, since a thorough system of ventilation produced by forcing air through the mine prevent the accumulation of this explosive gas.

Chlorine will decompose the gas, setting free the carbon and



uniting with the hydrogen to form hydrogen chloride. It requires 2 vols. of chlorine to decompose 1 vol. of methane, and the volume of hydrogen chloride formed is one and one-third times the sum of the volumes of mixed gases, or twice the volume of the chlorine used. No other products than hydrogen chloride and carbon are formed.

When the pure methane is acted on by the electric spark, under proper conditions, carbon is set free and is found on the platinum poles, while the gas left is pure hydrogen. The volume of the hydrogen is double that of the original volume of the methane.

**History and Name.**—This compound has received many names, some of which have been already given. It might properly be called hydrogen carbide, but there are a large number of compounds of hydrogen and carbon, and the ordinary system of naming compounds is not used. These compounds are all known under the general name of hydrocarbons. This is the simplest hydrocarbon known. The name methane is derived from the word *methyl*, a name applied to an alcohol produced by the destructive distillation of wood. The word *methyl* literally means the *wine*, or *spirit*, of *wood*; that is, something that comes from wood in the form of a gas. Methane is closely connected with methyl alcohol, but a study of this compound, however, belongs to organic chemistry.

Methane has been known from the earliest time, but was not distinguished from hydrogen until the year 1776. In 1785 its composition was shown to be carbon and hydrogen only.

*Formula of Methane and the Atomic Mass of Carbon.*

**Facts.**—(1) **Of Quantitative Analysis.**—**Experimental Study, No. 37.**—(a) Pass into an explosion burette, or Ure's eudiometer tube, say 10 cc. of pure methane, then pass in 25 cc. of pure oxygen. Pass the spark and notice the volume of the

gas left in the tube. Now, by means of a pipette, pass into the tube 10 cc. of potassium hydroxide solution. The potassium solution absorbs carbon dioxide, forming with it a soluble compound. (See page 296.) Notice the volume of the gas left and prove that it is pure oxygen. Where is the hydrogen? If this experiment is made using a jacketed explosion burette, the gaseous volume of the water formed can be measured. With the volumes of the gas given, — that is, 10 cc. of methane and 25 cc. of oxygen, — the gases remaining after the explosion will have a volume of 35 cc., of which 5 cc. is oxygen. If now potassium hydroxide is introduced, the volume is reduced by 10 cc., leaving 20 cc. of water vapor.

(*b*) Slowly pass a definite volume of methane over red-hot copper oxide contained in a combustion tube. The products are absorbed and weighed. The water is absorbed in a tube containing either calcium chloride or sulphuric acid, and the carbon dioxide is absorbed by potassium hydroxide (KOH) solution contained in a special tube. The tubes are weighed before and after the absorption, and the amount of hydrogen and carbon calculated from these results.

It has been shown that this gas consists of carbon and hydrogen only, and that when a given volume is decomposed by the electric spark the carbon is set free as a solid, and that the volume of the hydrogen is double that of the original volume of the gas taken.

What will 100 cc. of the gas weigh under standard conditions? What is the volume of hydrogen formed when this volume is decomposed? What will this volume of hydrogen gas weigh under the same conditions? Show that the per cent of carbon is 74.95, and that the per cent of hydrogen is 25.05.

The per cent of carbon and hydrogen may be calculated from the facts determined by (*b*). Take, for example,  $\frac{1}{2}$  l. of methane. Under standard conditions it will have a mass in grammes of  $.0896 \times 7.98 \div 2 = .3575$  g. The calcium chlo-

ride tube under these conditions gained .8053 g. in mass, and the potassium hydroxide tube gained in mass .983 g., or this was the amount of carbon dioxide ( $\text{CO}_2$ ) that was formed in the experiment. It has been shown that  $\frac{1}{2}$  of water is hydrogen; therefore the  $\frac{1}{2}$  l. of gas contains what per cent of hydrogen? The per cent of carbon in carbon dioxide is 27.27; therefore what is the per cent of carbon in  $\frac{1}{2}$  l. of methane?

(2) The density of the gas is 7.98 (8).

(3) One volume of the gas contains 2 vols. of the hydrogen.

(4) No gaseous molecule of any carbon compound contains less of the element than this molecule.

By applying the method for determining the formula for a gaseous molecule, it is found that 11.97 parts of the molecule is carbon, and 4 parts are hydrogen. By using fact (4) the formula may be written  $\text{CH}_4$ , and the atomic mass of carbon is 11.97.

Show by study of fact (3) how it is probable that there are 4 atoms of hydrogen in the molecule of this gas.

**Another Method of showing why Methane may be considered to have Four Atoms of Hydrogen in its Molecule.** — When methane is treated with chlorine gas in diffused sunlight, it is decomposed, and two compounds are formed, one composed of hydrogen, carbon, and chlorine, and the other of hydrogen and chlorine or hydrogen chloride. The first compound contains the elements mentioned in the proportions by mass of 3 parts of hydrogen to 35.37 parts of chlorine to 11.97 parts of carbon.

By means of direct sunlight the following compounds are formed: —

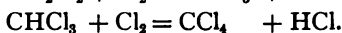
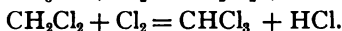
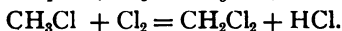
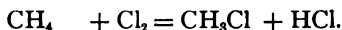
(1) A compound containing 2 parts of hydrogen, 70.74 parts of chlorine, and 11.97 parts of carbon is produced.

(2) A compound containing 1 part of hydrogen, and 106.11 parts of chlorine, and 11.97 parts of carbon is formed.

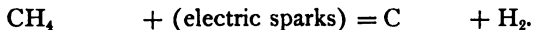
(3) A compound without hydrogen, but containing 141.48 parts of chlorine and 11.97 parts of carbon. Each of these compounds can be changed back to methane by treating them with nascent hydrogen. In each of these four reactions a single molecule of hydrogen chloride is formed.

It will be noticed that the hydrogen has been divided into four equal parts, each part being replaced by 35.37 parts of chlorine, showing that there are at least four parts, or four atoms of hydrogen to the molecule of methane.

These reactions may be written thus : —



Other reactions : —



Explain each equation, and balance when necessary. Read each equation by volume and by mass.

**Problems.** — How many litres of hydrogen sulphide will be required to prepare 10 l. of methane?

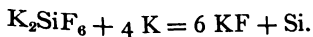
How much copper oxide will be required to decompose 20 l. of marsh gas? Express the amount of the products by volume, and also determine it by mass.

**SILICON.**

**Distribution and Occurrence.** — Silicon does not occur free in nature, but is found in large quantities combined with oxygen as silicon dioxide. Silicon dioxide in its more or less pure form is known as sand. Combined with oxygen and with such metals as sodium or potassium and aluminum, under the name of silicate, it forms a large part of the earth's crust. It is next to oxygen the most abundant element in the earth's crust. Some of the common substances containing silicon are silicon dioxide, sand, quartz, and silicates occurring in granites and clays. Quartz exists as sand, flint, jasper, agate, and rock crystal. It is, in fact, the principal substance in nearly all rocks, if coal and limestone be excepted.

**Methods of Preparation.** — The element silicon is not readily obtained from the common compound (silicon dioxide), although it can be obtained from it by means of the electric furnace. It may also be prepared by heating the oxide with the metal potassium. It is most commonly prepared by heating a compound of potassium, silicon, and fluorine (the compound having the formula  $K_2SiF_6$ ) with potassium or with potassium and zinc.

**Preparation.** — Mix 10 g. of dry finely powdered potassium silicofluoride ( $K_2SiF_6$ ) with three-fourths its weight of metallic potassium, and heat to red heat in either a hard glass tube or (better) a clay crucible. The potassium should be cleaned and cut in small pieces. The following reaction occurs : —



Explain why the action occurs. Explain from a chemical and physical standpoint.

Potassium fluoride (KF) is soluble in water, while the silicon is **not**; and the silicon is separated by filtering the latter out.

If metallic zinc is added to the molten mass formed by the above method, and the heat continued until the zinc fuses, it dissolves the silicon. When the mass cools, the silicon separates out in a needle-like crystal. The zinc is removed by hydrochloric acid.

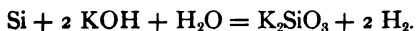
If the potassium silicon fluoride ( $K_2SiF_6$ ) is heated with the metal aluminum, the silicon separates out, when the mass cools, as a black crystalline mass much resembling graphite; hence it is called graphitoidal silicon.

**Physical Properties.** — Silicon exists in two forms — the amorphous and the crystalline. The crystalline silicon is either in the form of steel-blue needle-like crystals or in a form resembling graphite.

The amorphous variety is of a brown color and exists in a fine powder, but when heated for a long time at a high temperature it is converted into the crystalline variety. The crystalline variety is a very hard substance, so hard that it readily scratches glass. They are all fusible at a very high temperature. Silicon is insoluble in water and does not conduct electricity.

**Chemical Properties.** — The amorphous silicon has great affinity for oxygen, and when heated in the air, unites with its oxygen with great rapidity and produces a high temperature. The crystalline forms do not unite with oxygen even when heated to high temperatures. None of the forms of silicon are acted upon by the ordinary acids; that is, by hydrochloric, nitric, and sulphuric acid. The brown variety is dissolved in hydrofluoric acid (HF), while the crystalline variety is only dissolved by hydrofluoric and nitric acid acting together. It unites with dry chlorine gas by the aid of heat.

All varieties dissolve in potassium hydroxide according to the following reaction: —



**History and Uses.** — In the last part of the eighteenth century Lavoisier suggested that silica was a compound substance. In 1810 Berzelius prepared silicon from silica by fusing it with iron and carbon. The method now commonly used in preparing the amorphous variety was described by him in 1823.

As an element it has no particular uses. It, however, plays an important part as an alloy in iron and steel manufacture.

*Compound of Hydrogen and Silicon, or Hydrogen Silicide.*

**Methods of Preparation.** — Silicon does not unite directly with hydrogen, but when the alloy of silicon and magnesium is treated with hydrochloric or sulphuric acid, hydrogen takes the place of the magnesium and hydrogen silicide is formed. The product, however, is impure, being mixed with free hydrogen.

It can be prepared in a pure condition by treating triethylsilicoformate ( $\text{Si}(\text{OC}_2\text{H}_5)_3\text{H}$ ) with sodium.

**Preparation.** — Mix thoroughly powdered glass and finely divided magnesium. Place the mixture in a narrow ignition tube and heat until the magnesium is fused. Magnesium silicide is formed. Cool, and remove the fused mass by breaking the tube. Put the fused mixture in an evaporating-dish and treat with concentrated sulphuric acid. The gas that is formed ignites spontaneously on coming in contact with the air. Collect sufficient amount of gas to examine its physical properties. The gas thus made contains free hydrogen.

A purer gas can be made by placing in a red-hot clay crucible 18 g. of sodium fluosilicate, 20 g. of magnesium chloride, 5 g. of sodium chloride, and 10 g. of sodium. These substances are thoroughly dried and mixed. The crucible is covered immediately on adding the mixture, and the heat con-

tinued until chemical action ceases. When cool, the mass is broken up and placed in a generator bottle which is filled with recently boiled but cooled water. The conducting tube is also filled with water which is free from air. Hydrochloric acid is now added through the funnel tube, and the gas is collected over water, which must be free from air.

**Experimental Study, No. 38.** — (a) Examine the gas for its physical properties.

(b) If pure gas can be had, compare the action of air on it with the action of air on the impure gas.

(c) Treat a portion of the gas (say 10 cc.) with a solution of potassium hydroxide. Examine the gas that remains. What is it?

(d) Heat a portion of the gas in a closed tube; cool and examine the products, noticing the volume—that is, under original conditions. (The gas used for this experiment should be pure.)

(e) Allow the gas made from the magnesium compound ( $\text{Mg}_2\text{Si}$ ) to escape into the air. Explain the flame and the white fumes that are formed, knowing that the escaping gas consists of silicon and hydrogen.

(f) If possible, test the pure gas in the same way. Bring a burning stick near the escaping gas.

(g) Place a bottle of the gas mouth uppermost; open it, and bring near it a burning stick or a red-hot wire. What is the deposit on the sides of the bottle? Prove that water is another product.

(h) Pass dry chlorine gas into a bottle of the hydrogen silicide.

**Properties.** — Hydrogen silicide is a colorless gas, about as heavy as oxygen. It is decomposed at red heat into hydrogen and silicon. Potassium hydroxide solution forms potassium silicate ( $\text{K}_4\text{SiO}_4$ ) and hydrogen. When decomposed in this manner, one volume of the gas yields four volumes of hydrogen,



same general composition as ordinary chloroform, silicon taking the place of carbon in the molecule. Its vapor density is 68.

**Resemblances of Silicon to Carbon.**—Carbon and silicon resemble each other in both their physical and chemical properties. Silicon exists in three forms, corresponding to the three forms of carbon; that is, to the amorphous, graphitic, and diamond forms. The amorphous variety of silicon readily takes oxygen and forms a compound ( $\text{SiO}_2$ ) corresponding to  $\text{CO}_2$  of carbon. The crystalline varieties are hard and do not oxidize even at high temperature, thus resembling graphite and the diamond. They are not attacked by acids and form similar compounds with the halogens. Many other compounds of the two elements are closely related, as will be evident when these compounds are examined later on.

---

### RECAPITULATION.

Up to this point we have studied the element hydrogen, the halogens, the sulphur group, nitrogen, phosphorus, antimony, carbon, and silicon. We have especially studied the physical and chemical properties of these elements, and in each case the compound that the element formed with hydrogen and in many cases the compounds formed with the halogens.

**The Foundation Truth. — The Law of the Conservation of Matter.**—It is the statement of the fact so far as observation has determined it, that the total mass of the substances taking part in any chemical change remains constant.

An examination of the various chemical compounds both by synthesis and by analysis shows that the composition of any given compound is always constant,—the law of definite proportions. This law is supplemented by the law of multiple proportions.

An attempt to explain these laws—that is, to find their cause or causes—leads to the atomic constitution of matter. All chemical facts harmonize with this conception of the constitution of matter. The conception of the atomic constitution is not based on our knowledge of the ultimate constitution of matter, but it is a method of comprehending, or picturing to ourselves, the method of the action of matter when it undergoes chemical change. This atom thus becomes the unit of chemical change, and the mass of this unit was, historically speaking, next sought. It is evident that its mass according to our common standards of mass measure cannot be determined, since the number of these units in a given portion of matter has not been, and perhaps cannot be, accurately determined. Hence only relative atomic masses can be determined. It is understood that all chemical changes are among atoms, and that groups of atoms, produced according to chemical laws, called molecules, are the units of mass. It is therefore through a study of this unit of mass that we can determine the relative mass of atoms. Analysis and synthesis can only give the percentage of each element in the molecule. As for example, an analysis of hydrogen chloride shows that it contains 97.25 per cent of chlorine and 2.75 per cent of hydrogen, or taking the amount of hydrogen as unity, it shows that there are 35.37 parts of chlorine to one part of hydrogen. But this does not tell us whether there is one atom of hydrogen or any other number of atoms.

This is true, however, that there is for each element a fixed quantity or some multiple of this fixed quantity that enters into all compounds of which it may form a part. If, therefore, some element is chosen as unity, the combining mass of all the others may be expressed as ratios to this mass. An element should be chosen therefore that enters directly into combination with the greatest number of other elements. Oxygen represents best such an element, but, as we have seen, hydrogen

has been chosen. This element was chosen by Dalton because its atomic mass was evidently the smallest of all the others. A discussion of the objections to hydrogen as such a unit does not belong to this elementary work.

**Molecular Mass and Atomic Mass.** — The laws of Avogadro and Gay-Lussac give us the means of determining the molecular mass of all compounds that are gases or that can be converted into gases without decomposition. But since this is only a relative mass, some unit must be determined upon in order that each molecule may be measured by some standard unit. The hydrogen molecule is selected. Now when the mass of any definite volume of a gas is known (say for example 1 l.), we have immediately the relative mass of its molecule to that of a molecule of hydrogen. As has been seen, the best evidence is that there are two atoms in the hydrogen molecule. (See page 66.) Hence the number expressing the relative mass of the molecules is doubled for the molecular mass, since it is to be expressed in terms of the atom, or half-molecule of hydrogen. The percentage composition, therefore, enables the chemist to determine the amount of each element in the molecule in terms of the atom of hydrogen, or of the hydrogen half-molecule.

This naturally leads to the definition of an atom, as the smallest amount of any element found in any molecule. For example, the smallest amount of chlorine in any molecule has been found to be 35.37; for bromine, 79.96, etc. These numbers represent, therefore, the atomic mass of the elements mentioned.

It is therefore necessary, in order to determine the atomic mass of any element, to bring together the results of the analysis of as large number of molecules as is possible and to select from these the smallest amount of the given element as its atomic mass.

Examine, for example, the results of the analysis of a series of gaseous molecules of compounds containing chlorine.

COMPOUND.	VAPOR DENSITY.	MOLECULAR MASS.	PER CENT OF CHLORINE.	MASS OF CHLORINE.
Hydrogen chloride . . . .	18.185	36.37	97.25	35.37
Methyl chloride . . . . .	25.17	50.34	70.26	35.37
Mercuric chloride . . . . .	135.37	270.54	26.14	70.74
Boron trichloride . . . . .	58.55	117.11	90.60	106.11
Silicon chloride . . . . .	84.75	169.5	83.464	141.48
Phosphorus trichloride . . .	68.535	137.07	74.41	106.11
Oxychloride of chromium . .	77.43	154.86	45.67	70.74
Arsenic trichloride . . . . .	90.5	181.00	58.62	106.11

An examination of this table shows that there is no molecule containing less than 35.37 parts by mass, and that all other masses are multiples of this mass. This is taken as the atomic mass of chlorine. Similar tables can be made for all other elements that form gaseous compounds, and thus the smallest amount of the element under consideration may be determined from these molecules.

The molecular mass of any gaseous substance is the mass of that substance which occupies the same volume as does two parts of hydrogen, or what is called the molecule of hydrogen. This volume in terms of our usual units depends on the number of molecules in the standard of volume, the cubic centimetre, under standard conditions. The unit volume is space occupied by a molecule of any gas under standard conditions. The term *occupied* means, as here used, that each molecule of a gaseous substance may be said to have set apart for it a certain definite space, the dimensions of which will vary with the temperature and pressure to which the gas is subjected; but for the standard conditions, or, in fact, for all like conditions

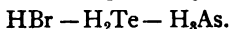
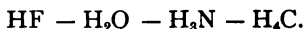
in reference to these two factors, this volume is the same for all true gases. It is not meant that the molecule fills completely this unit volume, but since all true gases under like conditions contain the same number of molecules, this space must be alike for all such gases.

**Size and Number of Molecules.** — It is not intended to discuss here the methods by which the size and number of molecules in any volume of gaseous matter have been determined, but merely to state the conclusions reached by such investigators as Maxwell and Sir W. Thomson.

It has been determined that molecules differ in size, but that the average diameter of those already studied is about the eight-millionth part of a millimetre.

The number of molecules in a cubic centimetre of gas, as estimated by different investigators, varies within certain limits. (The principles that are made use of in these determinations are not questioned, but the details of the methods used are yet subjects of discussion.) The number commonly accepted as expressing the number of molecules in the cubic centimetre is  $21 \times (10^{18})$  under standard conditions.

**Valence.** — If we compare the formulæ of the compounds studied thus far, it will be found that they can be arranged in four classes, on the basis of the number of atoms of hydrogen uniting with the atom of each of the elements. The groups are

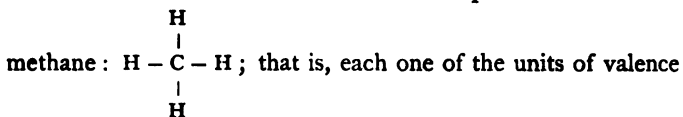


These are the only stable compounds that hydrogen forms with these elements. These molecules are said to be saturated; that is, they have taken up all the hydrogen that they can hold in combination under ordinary conditions. It will

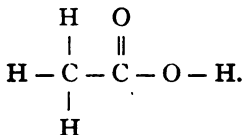
be noticed that the elements of the first group hold one atom of hydrogen, those of the second group hold two atoms, those of the third group hold three atoms, while those of the fourth group hold four atoms of hydrogen. Other elements possess the same property; that is, the property of holding a certain definite number of atoms or groups of atoms in combination. This property is called valence. The valence of hydrogen is taken as unity, since it forms but one stable compound with any of the elements. It does not unite with a large number of the elements, and consequently the valence of the elements with which it does not form compounds must be determined by considering the compounds of these elements with others that do unite with hydrogen. For example, sodium does not unite with hydrogen ordinarily, but it does unite with chlorine; and, as we have seen, one atom of hydrogen unites with one atom or 35.37 parts of chlorine, but 23 parts of sodium unite with 35.37 parts of chlorine. Since 23 parts of sodium is the atom of sodium, it is said to have the same valence as chlorine, and consequently the same as hydrogen. The valency of the elements is indicated by the words *univalent*, or the element is said to be a monad; *divalent*, or the element is said to be a dyad; *trivalent*, or the element is a triad; *tetravalent*, or the element is a tetrad; and so on, using the Greek numerals to indicate the higher valencies. Chlorine is thus said to be univalent or a monad; oxygen, a dyad, etc.

These facts are commonly represented to the eye by straight lines or dashes written in connection with the element (*e.g.* the divalence of oxygen is represented  $\text{—O—}$ ), or the same idea is indicated by means of Roman numerals written to the right and a little above the symbol of the element; *e.g.*  $\text{O}^{\text{II}}$ . The meaning of this representation is that the atom-fixing power may be considered as divided into units and that oxygen possesses two of these units. In all compounds the units of the valence of its

elements are saturated. This fact is represented thus for



of carbon is satisfied by the single atom of hydrogen. Representations of compounds in this manner constitute structural formulæ. The beginner must guard against the notion that these representations indicate the space arrangement of atoms. They are aids in understanding and in illustrating how the atoms are grouped; that is, what atoms are probably united together in the compound, or at least it shows the way the elements leave and enter the compound when studied analytically or synthetically. Such formulæ are of great service, especially in the study of complex molecules. The formula for acetic acid, for example, may be written  $\text{C}_2\text{H}_4\text{O}_2$ , or



The former expression says that the molecule is composed of two atoms of carbon, four atoms of hydrogen, and two atoms of oxygen, but says nothing of how these atoms are united in the molecule. The latter expression says the same, and in addition, that the compound contains the groups  $\text{CH}_3$ ,  $\text{CO}$ , and  $\text{OH}$ . This latter fact has been learned by careful analysis and synthesis of this compound.

The cause of valence has not yet been determined; but whatever the explanation of the facts may be, their application to the formulæ of chemical compounds is of great service to the student, aiding him in remembering and writing formulæ.

Although valence is constant in reference to hydrogen and the elements with which it unites, it is apparently variable with

reference to other elements, as will be seen later on ; but if we consider the valence of oxygen as fixed at 2, the variability of other elements in this regard is easily remembered and kept within narrow limits.

*Compounds of Sulphur with Oxygen and with Oxygen and Hydrogen.*

**Methods of Preparation. — Sulphur and Oxygen. — Sulphur Dioxide.** — Sulphur unites directly and readily with oxygen when heated to a temperature of  $160^{\circ}$ , producing a gaseous compound. It is also prepared by the action of sulphuric acid on such metals as copper and mercury, and also by its action on carbon.

**Preparation.** — (a) *From Elements.* Place about 1 g. of sulphur in the deflagrating-spoon ; ignite it, and place it in a gas-bottle full of air or (better) full of pure oxygen. When action ceases, remove the spoon and cover the bottle tightly. Fill in this way two or three bottles.

(b) *From Sulphuric Acid and Copper.* Place 15 g. of copper turnings or filings in a 100 cc. flask or large test-tube, and add sufficient concentrated sulphuric acid to cover them. Prepare for collecting the gas by downward displacement in dry bottles. Note first whether there is any action in the cold, and if so, its general character. Next, heat the generator until the gas escapes with sufficient rapidity, and then heat only sufficiently to keep up this flow of gas. Collect the necessary number of bottles of gas. Also pass the gas into 100 cc. of water for five minutes, then pass it into a dilute solution of potassium hydroxide (KOH) to which a little litmus solution, or phenolphthalein solution, has been added, noticing the effect on the indicator. Pass the gas until the indicator changes. Save all these solutions for further examination.



**Experimental Study, No. 39.** — (a) Examine the gas for common physical properties, e.g. odor, and with dry and moist litmus paper.

(b) Add to a bottle of gas 100 cc. of water. Close tightly with the palm of the hand, or with a rubber stopper, and shake well. Remove the hand, holding the mouth of the bottle under water.

(c) Attempt to pour the gas on a burning stick held near the mouth of the bottle. Explain what happens. Why does the stick cease to burn? Of what must the gas made by the method (a) be composed?

(d) Test another bottle of gas with a burning stick in the usual way.

(e) Place in a bottle of the gas a piece of magnesium wire. Do this when the wire is cold and when it is ignited. Explain the difference in the action. Which of the elements of the gas compound unites with magnesium? Explain this.

(f) Place flowers (for example, violets) free from external moisture in the dry gas for two or three minutes; moisten, and place in the gas for five minutes. Remove the flowers, and dip one in a dilute solution of ammonia, and another in dilute chlorine water.

(g) Unbleached straw and woollen yarn should be treated in the same manner. After the woollen yarn has been exposed to the gas for some time dip it in a very dilute solution of potassium hydroxide. Account for the changes that occur in the color of the yarn.

(h) Bring together 1 vol. of this gas with 2 vols. of hydrogen sulphide, thoroughly mixing them, and ignite. Examine the products and explain the reaction. Arrange the elements of these compounds according to strength of their affinities.

(i) Examine the water solution as follows: —

1. To 10 cc. of a solution of potassium iodate ( $\text{KIO}_3$ ) add 2 cc. of carbon disulphide ( $\text{CS}_2$ ), and then add a few drops of

the solution, and shake. Explain. (The same result may be produced by passing the gas into the iodate solution. Turn off the clear liquid and test it for sulphuric acid.) (See page 225.) (A full explanation of this test cannot be made until sulphuric acid has been studied.)

2. Boil 10 cc. of the solution and examine the escaping vapor by the nose and by litmus paper. Explain.

3. To 10 cc. of the solution add 2 cc. of barium chloride solution. Follow by same amount of hydrochloric acid.

4. To 10 cc. of the solution add a few drops of hydrochloric acid and then a little of the barium chloride solution, and note the result. Now add 5 cc. of chlorine water, and warm, and note the result. What is the action of chlorine on water? How will the product affect the sulphurous acid? (See under SULPHURIC ACID for explanation.)

5. Make the neutralization experiments in the same manner as has been previously described. (See page 97.)

(*f*) Evaporate to dryness the solution of the gas in potassium hydroxide. Examine the residue by treating a portion with hydrochloric acid and warming. What gas escapes?

(*g*) Pass the dry gas (dried by passing it through sulphuric acid) through a tube surrounded by a freezing mixture, such as powdered ice and salt. (Special tubes are usually prepared and used for this purpose. The condensing tubes are usually furnished with stop-cocks, so that the liquefied gas may be kept without evaporation.) It is well to pass the gas through cool tubes before bringing it into the vessel surrounded by the freezing mixture.

**Physical Properties.** — Sulphur dioxide is a colorless gas having a characteristic odor. It can be converted into a colorless liquid by reducing its temperature to  $-8^{\circ}$  under 760 mm. of pressure. At  $-76^{\circ}$  it becomes a solid. It is readily absorbed by water, 1 vol. of water absorbing 50 vols. of gas under standard conditions. The solution is acid to litmus

paper, but the gas escapes on boiling the water. It is 2.24 times heavier than air, and its density is 31.96.

**Chemical Properties.** — This gas does not support ordinary combustion, but will yield its oxygen to magnesium at the temperature of ignition in the air, the sulphur being set free. It is a bleaching agent, although less active than chlorine. In all cases water must be present before bleaching action takes place. If the gas is mixed with hydrogen sulphide and ignited, sulphur is set free, and water is formed. It acts as a poison when inhaled, producing irritation of the throat and lungs, and when used in sufficient quantity produces suffocation and even death. It readily takes oxygen from the air, or from compounds that yield oxygen quite readily if moisture is present. Its water solution is acid, and it neutralizes bases, forming a solid substance or a salt.

Sulphur and oxygen form but one compound by direct union, but in the presence of water it does take up another atom of oxygen. In many cases of bleaching it is probable that the sulphur dioxide takes oxygen from the coloring matter of the article bleached, thus permanently destroying the coloring substance. Again, the coloring matter is evidently not destroyed, since this color is restored in course of time or by the action of some chemical agent. Straw and woollen yarn assume their original colors on exposure for a longer or shorter time to the atmosphere. The white wool assumes its original color when washed, and especially when soap is used in the washing; that is, when it is treated with an alkaline substance. In such cases it is probable that the colored compound unites with the sulphur dioxide in the presence of moisture, forming a colorless compound that is decomposed under the conditions mentioned.

*Determination of the Formula for the Compound of Sulphur and Oxygen.*

**Experimental Study, No. 40.** — A eudiometer like Fig. 10 is employed to determine the amount of oxygen in the compound. The cup *a* is filled with sulphur best by melting a fragment of sulphur in the cup. The apparatus is filled with mercury, and a sufficient quantity of pure oxygen gas is run into the tube; the pressure is equalized in both limbs, and the volume of oxygen noted. The pressure on the gas is next reduced by removing about one-third of the mercury. The open limb should now be stopped. The sulphur is next ignited by the electric current, when the sulphur will unite with the oxygen, the action continuing as long as any of the oxygen remains. The apparatus is allowed to return to the original temperature when sufficient mercury is added to restore the original pressure. It will then be found that the volume of the new compound is (nearly) the same as that of the original oxygen. When the action begins, there is formed a small amount of sulphur trioxide, — a solid body, — which slightly reduces the volume.

The following are the facts for the determination of the formula of the compound: —

(a) It consists of sulphur and oxygen alone.

(b) When decomposed, or when formed from oxygen and sulphur, the volume of the gas and the volume of the oxygen are equal. From these facts the percentage composition in connection with the density of the gas can be determined.

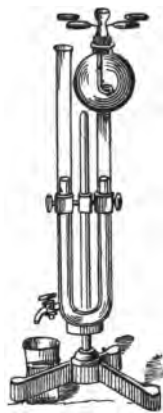


FIG. 10.

(c) Its density is 31.96.

(d) The atomic mass of each element is known.

**Problem.** — Using 1 l. of the gas, determine in connection with the facts just stated the percentage composition of the compound. From the percentage composition and the other facts, show that the formula for the compound is  $\text{SO}_2$ .

**Detection of Sulphur Dioxide.** — This gas can be detected by its odor, by its bleaching action, and by its action on a solution of potassium iodate.

**Uses of Sulphur Dioxide.** — This compound is used for bleaching straw, wool and woollen goods, and silk. The material to be bleached must be moist, and, as has been shown, it bleaches by taking oxygen either from water or from the coloring matter of the substance to be bleached, setting hydrogen free, and forming sulphuric acid. The hydrogen unites with the coloring matter in many cases, forming a colorless compound or compounds. In case of many coloring matters, the sulphur dioxide probably forms colorless compounds with them. (Compare its action with that of chlorine.)

The gas is also used as a disinfectant; it stops putrefaction and fermentation, and is therefore used as a preservative in case of liquids and solid organic substances that are attacked by the various organisms that set up these changes. It is said to destroy these organisms. Its action in disinfecting rooms, clothing, etc., used by persons suffering from scarlet fever, diphtheria, etc., is to destroy the organisms supposed to be directly, or indirectly, the cause of the disease. Great care, however, is necessary in using this disinfectant if thorough disinfection is required. It is necessary to know the length of time of exposure to, and the quantity of gas that is sufficient to kill all the germs. It requires, at least, 1.5 k. of sulphur for every one thousand cubic feet of air disinfected, that is, when the dioxide is made by oxidizing sulphur. Another essential is that moisture be present,

## REACTIONS.

- (a)  $S_2 + O_2 = SO_2$ .  
 (b)  $Cu + H_2SO_4 = CuSO_4 + H_2$ .  
 (c)  $H_2SO_4 + H_2 = SO_2 + 2 H_2O$ .  
 (d)  $C + H_2SO_4 = SO_2 + CO_2 + H_2O$ .  
 (e)  $H_2O + SO_2 = ?$   
 (f)  $Mg + SO_2 = MgO + S$ .  
 (g)  $H_2S + SO_2 = S +$   
 (h)  $2 KIO_3 + 5 SO_2 = 2 K_2SO_4 + 2 I + H_2SO_4$ .  
 (i)  $H_2SO_3 + BaCl_2 = BaSO_3 + HCl$ .  
 (j)  $H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2 HCl$ .  
 (k)  $H_2SO_3 + KOH = K_2SO_3 +$   
 (l)  $K_2SO_3 + HCl = KCl + SO_2 +$

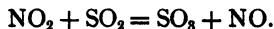
Explain each of these reactions ; read each of them by mass, and where gaseous molecules are produced, read them by volume.

**Problems.** — How much copper would be required to prepare 10 l. of sulphur dioxide?

How much sulphur dioxide by volume will be required to decompose 20 l. of hydrogen sulphide?

## SULPHUR TRIOXIDE.

**Methods of Preparation.** — Under normal conditions only one compound of sulphur is formed, but when the sulphur dioxide ( $SO_2$ ) is brought under proper condition, it takes up more oxygen. Such a reaction takes place, for example, when the dry gas mixed with oxygen is passed over heated platinum sponge. Explain why. It also occurs when sulphur dioxide is brought in contact with compounds which readily yield oxygen. For example, when nitrogen dioxide and sulphur are brought together, the following reaction takes place : —



If now oxygen is furnished to the nitric oxide ( $\text{NO}$ ), it takes up another atom of oxygen and becomes  $\text{NO}_2$ . This, in turn, yields the oxygen to the sulphur dioxide, the process being repeated as long as there remains any sulphur dioxide and oxygen.

**Preparation.** — Prepare dry sulphur dioxide and mix it with dry oxygen gas, using about 2 vols. of dioxide to 1 vol. of oxygen. Air may be used if it has been dried. Pass into this mixture dry nitric oxide prepared from copper and nitric acid, as described on page 237. Continue to pass in the gas as long as brown fumes are formed. It is well to have the apparatus so arranged that the gases can be mixed at once and continuously.

**Experimental Study, No. 41.** — (a) Heat some of the solid oxide in a test-tube and examine the deposit on the side of the tube with dry litmus paper. Note the result.

(b) Leave a portion of the solid substance exposed to the air for a short time. What becomes of it? Test what is left on the tube with litmus paper.

(c) Treat the remainder of what was prepared with water, and examine the solution with litmus, and by taste. Note the effect on the temperature of the water.

(d) Evaporate a portion of the water solution, noting any changes as the water escapes.

(e) Treat two or three definite volumes of the solution, say 5, 10, and 15 cc., with a standard solution of potassium hydroxide. Pour the resulting solutions together and evaporate to dryness. Examine the residue. Does it differ from the solid oxide? How? Examine a water solution of the solid as described under (b).

(f) Treat another portion of the acid solution with a solution of barium chloride ( $\text{BaCl}_2$ ). Add hydrochloric acid to this and warm. Compare with a similar experiment with the water solution of sulphur dioxide. (See (i), Experimental Study, No. 39.)

(g) Pass the vapor of the oxide through a red-hot tube and allow the escaping gas to pass into potassium iodate solution. What is the escaping gas? Bring a glowing coal into the escaping gas. Explain the result.

**Properties of Sulphur Trioxide.** — Sulphur trioxide is a crystalline solid, the form of the crystal depending, it is said, on whether the oxide is absolutely free from water or whether a small amount is present. When a small amount of water is present, it melts at  $16^{\circ}$  and boils at  $46^{\circ}$ ; but if absolutely free from water, it melts at  $14.8^{\circ}$  and boils at  $46^{\circ}$ . Its vapor density is 39.9. It unites readily with water, the reaction being accompanied with a marked rise in temperature. The dry oxide does not redden dry blue litmus paper. Its combination with water cannot be broken up at boiling temperature. When the vapor is heated to red heat, it is decomposed, yielding 2 vols. of sulphur dioxide and 1 vol. of oxygen.

**Formula for Sulphur Trioxide. — Facts.** — (a) It consists of sulphur and oxygen alone.

(b) It is produced by the union of 2 vols. of sulphur dioxide and 1 vol. of oxygen; the product occupies 2 vols. under the same conditions. Again, when the vapor of the oxide is decomposed, 2 vols. of the vapor yield 2 vols. of sulphur dioxide and 1 vol. of oxygen. (The percentage composition can be calculated from these facts by determining the amount of sulphur and oxygen in 2 l. of sulphur dioxide and adding to the mass of the oxygen the mass of 1 l. of oxygen under standard conditions.)

(c) The vapor density of the oxide is 39.93.

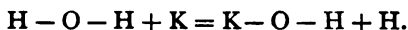
(d) The atomic masses of sulphur and oxygen are known.

**Problem.** — From the facts just given show that the formula for this compound is  $\text{SO}_3$ .

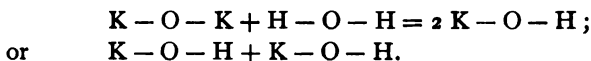
**Action of Water on the Oxides of Sulphur. — Acids of Sulphur.** — We have already seen that when potassium or sodium acts on water there is a compound formed by replacing one



of the atoms of the hydrogen of water by one atom of potassium or sodium, the hydrogen being set free. This fact is represented by the equation : —

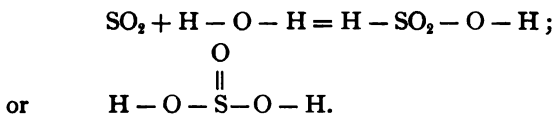


When the oxide of either of these bases is brought in contact with water, the same product is formed, but no hydrogen is set free. This reaction may be represented as follows : —

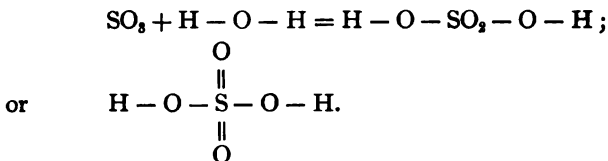


One of the atoms of potassium exchanges place with an atom of hydrogen.

Now when the oxide  $\text{SO}_2$  is brought in contact with water, the following reaction is supposed to occur : —



With the oxide  $\text{SO}_3$  the reaction is as follows : —



Here the sulphur is represented as having a valence of 4 in the first case and a valence of 6 in the second case. The arguments in favor of this structural representation are not properly considered here. It should be noticed, however, that these acid compounds are hydroxyl compounds like the basic compounds  $\text{KOH}$ ,  $\text{NaOH}$ , differing only in the atoms, or groups of atoms, that replace the hydrogen of water.

In general, it may be said that the usually formed oxides of the elements arrange themselves in two classes according to the action of water on them; that is, into those that form acids and into those that form bases. There are a few oxides of which this is not true.

It is interesting to notice that the elements are thus arranged in a double series in reference to the properties of acidity and basicity. If potassium is placed at one end of this series, representing the bases, and sulphur at the other end of the series, representing the acid, then all the other elements stand between them. These properties gradually decrease as we pass from either end of the series towards the other end. In the central portions of the series appear several elements that present either one or the other property, according to the amount of oxygen present in the oxide. The characteristic property of the series decreases in prominence as this central portion is approached.

It should be understood here that by placing sulphur represented by sulphuric acid at the head of the acid end of the series it is not intended to say that in all respects it is the most powerful acid. It is meant in the sense that sulphuric acid will decompose most of the salts of other acids, setting either the acid free as an acid, or forming products characteristic of the given acid, the hydrogen of the sulphuric acid being replaced by the base of the decomposed salt. Heat is often necessary to aid in the decomposition. Later on it will be shown that nitric acid is to be considered as the most powerful acid when viewed from another standpoint; *i.e.* from that of avidity, which is measured by the heat of neutralization.

**Valence of Sulphur.** — As has been shown, the valence of the element in reference to hydrogen appears to be fixed at 2, one compound only being formed. Now if oxygen is a dyad, then there should be but one compound formed containing sulphur and oxygen, and that should have the formula  $S = O$ .

(But this oxide does not exist, although an acid and its salts are known that may be said to correspond to it.) In the oxides  $\text{SO}_2$  and  $\text{SO}_3$  sulphur may be considered as having a valence of 4 and 6, respectively ; that is, if oxygen has a fixed valence of 2.

Many other elements will be seen to present the same peculiarity. In general, when there is variability in valence, it is towards oxygen or members of the halogen group, usually represented by chlorine. Again, it will be seen, as in this case, that the valence usually changes by twos ; that is, if an element has a valence of 1, any higher valence will be represented by 3, 5, 7, etc. If the lowest valence of any element is 2, and it has any higher valence, it is represented by 2, 4, 6, 8, etc.

Valence also varies with the temperature to which the elements forming the compound are subjected. For example, we have seen that phosphorus has a valence of 3 and 5 towards chlorine at ordinary temperatures, as is shown by the compounds having the formulæ  $\text{PCl}_3$  and  $\text{PCl}_5$ . If the compound  $\text{PCl}_5$  be heated to a temperature of  $100^\circ$ , it is converted into a gas, and is unchanged, chemically speaking. If, now, this gas is heated to  $300^\circ$ , it is decomposed into free chlorine ( $\text{Cl}_2$ ) and phosphorus trichloride ( $\text{PCl}_3$ ). In this case the phosphorus evidently has a valence of 3. Again, if this mixture of gases is heated to a sufficiently high temperature, the compound  $\text{PCl}_5$  is decomposed into free chlorine and phosphorus, and at that temperature the valence of phosphorus for chlorine can be said to be 0.

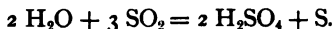
Generally speaking, the variability in valence is within narrow limits.

If valence is regarded as variable, then it cannot be considered as a property characterizing an element by itself, but as a property determined by the elements that may be brought together. To apply this to a particular case : When sulphur is brought into contact with hydrogen, two atoms unite with one

of sulphur, no more and no less ; but when sulphur is brought into contact with oxygen under proper conditions, two stable compounds are produced, represented by the formulæ  $\text{SO}_2$  and  $\text{SO}_3$ . Again, chlorine will be found to unite with one three, five, and seven atoms of oxygen forming four different compounds.

**Sulphurous Acid and its Anhydride.** — There are two oxygen acids of sulphur, and hence, according to the system of nomenclature previously given, they should be designated as sulphurous and sulphuric acid. The formula for sulphurous acid is commonly written  $\text{H}_2\text{SO}_3$ . One or both of the atoms of hydrogen can be replaced by bases forming salts, called sulphites. The two salts are distinguished by calling the one containing hydrogen the acid sulphite, and the one containing no hydrogen the normal sulphite. The term *acid salt* is generally applied to all salts in which only a part of the replaceable hydrogen of the corresponding acids is exchanged for a metal.

This acid is quite unstable, taking up oxygen from the air even, and becoming sulphuric acid ( $\text{H}_2\text{SO}_4$ ). In the sunlight it decomposes water, setting sulphur free.



**Determination of the Formula for Sulphurous Acid.** — Sulphurous acid has not been isolated from its solution in water. When the excess of water is evaporated off, the compound breaks up into water and sulphur dioxide. The formula has been determined by the study of its salts in connection with the facts known as to the formation, to its oxidation, and also by its analogy to other salts.

The facts as to its salts are : —

(a) It forms two salts with such bases as sodium and potassium. These elements, as we have seen, can replace hydrogen atom for atom.

(b) When these salts are analyzed (*e.g.* those of sodium), one salt is found to contain hydrogen, while the other contains no hydrogen, but does contain twice as much sodium as the first one.

(c) The amount of sulphur and oxygen is the same in case of both salts.

In 100 parts, or grammes, of the acid sulphite of sodium there are 22.115 parts by mass of sodium, .9615 parts of hydrogen, 30.77 parts of sulphur, 45.96 parts of oxygen. Dividing these numbers by the atomic masses of the corresponding elements, the results may be indicated thus:—

Sodium,  $22.115 \div 23 = .961 \div .961 = 1$ , or one atom of sodium.

Hydrogen,  $.961 \div 1 = .961 \div .961 = 1$ , or one atom of hydrogen.

Sulphur,  $30.77 \div 32 = .961 \div .961 = 1$ , or one atom of sulphur.

Oxygen,  $45.96 \div 16 = 2.872 \div .961 = 3$ , or three atoms of oxygen.

The formula for this salt may therefore be written  $\text{NaHSO}_3$ .

A similar examination of the normal salt shows that there are two atoms of sodium, corresponding to two atoms of hydrogen, one atom of sulphur, and three atoms of oxygen in the compound. These are the only salts that the acid forms with sodium. Bases similar to sodium,—that is, those that have a valence of one,—or all monad bases in general, produce the same two series of salts. Hence the formula for the normal salt is  $\text{Na}_2\text{SO}_3$ , and of the corresponding acid it is  $\text{H}_2\text{SO}_3$ .

#### SULPHURIC ACID OR HYDROGEN SULPHATE.

**Methods of Preparation.**—Sulphuric acid may be prepared by bringing sulphur trioxide ( $\text{SO}_3$ ) in contact with water according to the reaction—



This is practically the process used in its manufacture on

an extensive scale, the important point being the manufacture of the sulphur trioxide.

**Preparation.** — Fit up apparatus according to Fig. 11. *a*, *b*, and *c* are generating vessels. In *a* sulphur dioxide is generated by the action of sulphuric acid on copper or on carbon. In *b* nitric oxide is generated by the action of nitric acid on copper. In *c* steam is prepared. All three flasks are con-

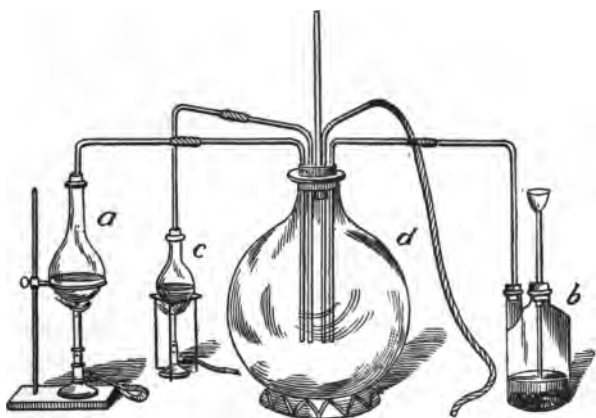
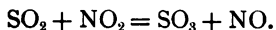


FIG. 11.

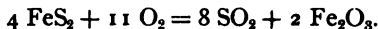
nected with a large flask (2 to 3 l.), *d*. *d* is closed by a stopper having a number of openings sufficient to admit delivery tubes from *a*, *b*, and *c*, to admit air, and to allow the escape of the gases.

When the proper connections are made, as indicated in the figure, the nitric oxide (NO) is first generated and driven into the flask *d* until it is filled with the brown gas (NO<sub>2</sub>). Next, sulphur dioxide is prepared and driven into the flask, when the reaction previously given occurs ; that is :—



If now more air is driven in the large flask, the nitric oxide (NO) becomes the dioxide ( $\text{NO}_2$ ), and immediately it yields the atom of oxygen gained from the air to sulphur dioxide. Steam is next admitted, and sulphuric acid is produced by the union of water with the trioxide. If all these substances are supplied simultaneously and in sufficient quantity, the process becomes continuous.

In the manufacture of the acid on a commercial scale the same process is used, only the sources of the substances are different. Iron pyrites ( $\text{FeS}_2$ ) is the source of the sulphur, the air and nitric acid supplying the oxygen. The pyrites is roasted, when its sulphur unites with the oxygen, forming sulphur dioxide.



This gas is driven into large leaden chambers, and at the same time nitric acid and steam enter the chamber and react with the sulphur dioxide, forming sulphuric acid and the oxides of nitrogen, mostly  $\text{N}_2\text{O}_5$ . The nitrogen trioxide forms a compound with sulphur dioxide with a small amount of water. This compound is decomposed by more water into sulphuric acid and nitrogen trioxide. The intermediate compound is represented by the formula  $\text{SO}_2 - \text{NO}_2 - \text{O} - \text{H}$ , called nitrosyl sulphuric acid. This is a compound in which nitrogen dioxide ( $\text{NO}_2$ ) takes the place of hydroxyl. These reactions are repeated so long as the dioxide and water and sufficient nitric acid is added to make up for any waste due to escape of gases.<sup>1</sup>

The acid accumulates in leaden chambers, but contains a large per cent of water, generally about 35. This water is removed by evaporation until only about 8 per cent remains. This product is the commercial sulphuric acid. The pure acid has a specific gravity of 1.854 at  $0^\circ$ .

---

<sup>1</sup> For drawings of the chambers, etc., see larger works, like Roscoe and Schorlemmer.

The pure acid of commerce usually has a specific gravity of 1.84, and contains from 98 to 99 per cent of acid, as,  $\text{H}_2\text{SO}_4$ .

**Experimental Study, No. 42.** — (a) Place in a beaker 25 cc. of water, and slowly pour in 35 cc. of sulphuric acid, stirring the mixture with a small thin test-tube in which there is about 5 cc. of alcohol. Note the effect on the alcohol. (Ordinary alcohol boils at  $81^\circ$  to  $85^\circ$ .) (Pour the acid into the water, never the water into the acid.)

(b) When the mixture (a) has cooled to the temperature of the surrounding air, measure its volume, and compare it with the volumes of the water and acid combined. Explain the result.

(c) Place 5 cc. of sulphuric acid in a test-tube or beaker, and stir it with a match or piece of pine wood. A large part of wood is cellulose, which is commonly represented by the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  or  $(\text{C}_6(\text{H}_2\text{O})_5)_n$ . Explain the action.

(d) To 5 g. of sugar add 5 to 10 cc. of acid, and warm slowly. Sugar has the formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  or  $\text{C}_{12}(\text{H}_2\text{O})_{11}$ . Explain the reaction.

(e) Dilute 15 cc. of acid with 6 to 8 cc. of water ; cool, and dip into the mixture an ordinary filter paper. Remove it after about twenty seconds, and rinse it thoroughly, finally in dilute ammonia hydroxide. Compare the result with parchment paper.

(f) Treat 10 cc. of the dilute acid (1 to 20) with a solution of barium chloride ( $\text{BaCl}_2$ ), and compare the result with a similar examination of sulphur dioxide and sulphurous acid, after adding sufficient hydrochloric acid to acidify the solution.

(g) Treat a solution of any sulphate (e.g.  $\text{Na}_2\text{SO}_4$ ) acidified with hydrochloric acid in the same way as (f).

(h) Determine the action of the acid on metals such as mercury and lead. Recall its action on copper and on zinc. Notice the effect produced at ordinary temperatures and at higher temperatures.



(i) Neutralize different volumes of dilute sulphuric acid with a standard solution of potassium hydroxide (KOH). Compare with examples of neutralization previously given. Evaporate the solutions to dryness. Redissolve the residue in a small amount of water, and allow the product to crystallize.

(j) Treat a solid sulphite, such as sodium sulphite, with a few drops of sulphuric acid. What gas escapes? Compare the result here with the action of sulphuric acid and the salts of all the other acids studied.

**Properties of Sulphuric Acid. — Physical. —** Pure sulphuric acid is a colorless, oily-appearing liquid at ordinary temperatures. The commercial acid contains several impurities, depending on the source of the materials from which it is made. It frequently contains lead sulphate ( $\text{PbSO}_4$ ), due to the action of the acid on the lead vessels in which it is concentrated. When water is added to the acid, most of the lead sulphate is precipitated out, since it is less soluble in water and acid than it is in the pure acid. The pure acid is concentrated in platinum or in glass vessels. It frequently contains arsenic, which is derived from the pyrites, which has been roasted to produce the sulphur dioxide. The oxide of arsenic which is produced at the same time is volatile, and passes over with the sulphur dioxide. The dark color of the commercial acid is due to organic matter which is decomposed by the acid and is held in solution. The pure acid is obtained from the commercial variety by distillation. When heated to about  $440^\circ$  the acid is apparently vaporized, but the vapor is a mixture of equal volumes of the trioxide and water. At higher temperatures it is decomposed into sulphur dioxide, free oxygen, and water. A stream of the acid striking on red-hot bricks furnishes oxygen after the mixed gases produced by the decomposition of the acid are passed through water to absorb the sulphur dioxide. When the acid is mixed with water and allowed to cool, the volume of the mixture is less than the sum

of the volumes of water and acid. The acid boils at  $338^{\circ}$ ; that is, when the ordinary acid is heated to this temperature, the distillate contains a compound having the formula  $\text{H}_2\text{SO}_4$  and a very little water.

**Chemical Properties.** — When sulphuric acid and water are mixed, there is produced a large amount of heat, — an indication that an action resembling chemical change has taken place. The acid has such an affinity for water that it absorbs it from the air, and is therefore used to dry air and other gases which contain water vapor.

When sulphuric acid and water are mixed in the proportion of one molecule of water to one molecule of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), 6272 calories of heat are given off. When 1600 molecules of water are added to one molecule of the acid, 17,850 calories of heat are evolved. It is thus seen that more than one-third of the heat of solution is given off on the addition of one molecule of water to one molecule of the acid. Further addition of water above the 1600 molecules produces only a slight rise of temperature.

When the mixture of water and acid containing about 15 per cent of water is cooled down to  $0^{\circ}$ , there are formed crystals that have the composition of one molecule of sulphuric acid and one molecule of water ( $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ). This compound is called a hydrate. The name *hydrate* is applied to compounds in which water appears to exist as such. Sulphuric acid forms three compounds with water. The three compounds or hydrates are represented according to this conception thus:  $\text{H}_2\text{O} \cdot \text{SO}_3$ ,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ .

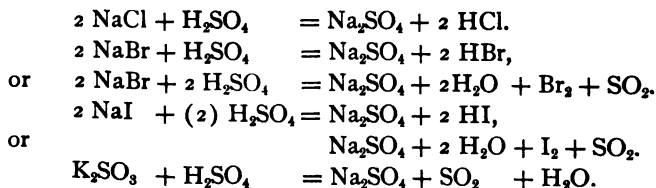
These compounds are sometimes represented as hydroxyl compounds. They are :—

Normal sulphuric acid ( $\text{SO}_2(\text{OH})_2$ ) — dihydroxyl sulphuric acid ;

Tetrahydroxyl sulphuric acid ( $\text{SO}(\text{OH})_4$ ) ;

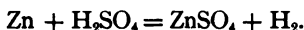
Hexahydroxyl sulphuric acid ( $\text{S}(\text{OH})_6$ ).

Only the sulphuric acid  $((\text{HO})_2\text{SO}_2)$  readily forms salts. When the other forms are treated with bases, the products are the ordinary sulphates. This great affinity of sulphuric acid for water is seen in its power to decompose many organic substances, such as sugar, cellulose, starch, etc. The formulæ previously given for cellulose and sugar must not be understood as meaning that they are carbon and water united. The hydrogen and oxygen in the compound are in the same proportions that they are in water, however. When these substances are brought in contact with sulphuric acid, water is removed and carbon is set free. Sulphuric acid decomposes the salts of most other acids, the products varying according to the salts decomposed; *e.g.* with chlorides, hydrogen chloride is formed; with bromides and iodides, hydrogen bromide and iodide are formed, but owing to the unstability of these acids at the temperatures produced, free bromine or iodine, and hydrogen are formed. If the temperature of decomposition is high, the nascent hydrogen attacks the sulphuric acid, forming water and sulphur dioxide. When sulphites are acted upon by sulphuric acid, the salt is decomposed, sulphur dioxide is set free, and a salt of sulphuric acid with the base is produced. In general, when sulphuric acids decompose salts, the corresponding sulphate is formed.

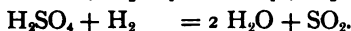
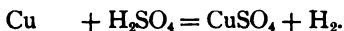


Upon metals, the action of sulphuric acid depends on the concentration of the acid, the metal acted upon, and the temperatures to which they are subjected. Upon some of the metals the dilute acid acts readily, producing a corresponding

sulphate and free hydrogen; e.g. the metal zinc. Other metals are but slightly attacked by dilute or by concentrated acid, unless heated, when a sulphate of the metal, water, and sulphur dioxide are formed. The reactions on zinc and copper represent, in general, its action upon metals.

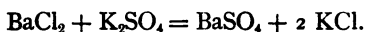


This last reaction is best represented in two stages, as follows:—



The nascent hydrogen at the temperature of the reaction (about  $300^\circ$ ) decomposes the acid, or takes from one molecule of it sufficient oxygen to form one molecule of water, setting sulphur dioxide free.

When sulphuric acid or some of its salts are treated with a solution of barium chloride, a white compound is formed, barium sulphate ( $\text{BaSO}_4$ ), which is insoluble in acids. This fact serves as a proof of the presence of free sulphuric acid, or of a sulphate in solution. (Exception: fluosilicic acid and its salts.)



Sulphurous acid and its salts are easily converted into sulphuric acid and sulphates by reagents that readily furnish oxygen, such as nitric acid. They slowly absorb oxygen from the air in the presence of moisture, and become sulphuric acid or sulphates.

**Tests for Sulphuric Acid and Salts.**—If the acid or salts are in solution in water, they are tested for by adding a solution of barium chloride and sufficient hydrochloric acid to make the solution distinctly acid. A white precipitate, insoluble in

the acid, indicates the presence of the acid, whether free or combined. Free acid may be recognized by its action on organic matter. Sulphates in the solid form may be recognized by fusing them on charcoal with sodium carbonate, and then removing the mass from the charcoal and testing for sulphide, according to methods given under tests for hydrogen sulphide. By this action the oxygen is removed from the sulphate, and the sodium of the carbonate combines with the sulphur, forming sodium sulphide.

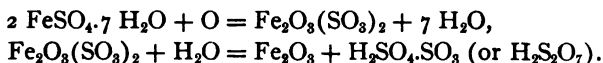
**Formula for the Acid and its Salts.**—The formula for the acid is determined in much the same manner as was that for sulphurous acid. The hydrogen of the acid is divisible into two parts, and into only two parts; that is, sodium forms two compounds or salts with the acid, one containing sodium, hydrogen, sulphur, and oxygen, and the other containing no hydrogen, but twice as much sodium and the same relative amount of sulphur and oxygen. Since an atom, or 23 parts, of sodium has been shown to replace one atom of hydrogen,—that is, it has a valence of 1,—it is considered that there are two atoms of hydrogen in the acid. On this basis there are 31.98 parts, or one atom of sulphur, and 63.84 parts, or four atoms of oxygen. The formula is therefore  $\text{H}_2\text{SO}_4$ . It forms both normal and acid salts with monad bases. The sodium and potassium salts accordingly have the formulæ  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KHSO}_4$ , and  $\text{K}_2\text{SO}_4$ , in the order named.

**Name and History of the Two Sulphur Acids.**—The two oxygen acids of sulphur, sulphurous and sulphuric acids, were the first to be studied, and are named according to the system of nomenclature. Sulphuric acid is also sometimes called hydrogen sulphate. It is known in commerce as oil of vitriol. It was so named by Basil Valentine, who prepared it from ferrous sulphate or green vitriol (glassy). The acid was made from ferrous sulphate exclusively until about the middle of the eighteenth century, when a process was invented by which it

was manufactured from sulphur and potassium nitrate ( $\text{KNO}_3$ ) or nitre. The present process of manufacture was first used during the last quarter of the eighteenth century.

**Uses.** — Sulphuric acid is perhaps the most important manufactured substance. It is used either directly or indirectly in nearly every branch of chemical industry. By its use nearly all other acids are prepared. In the manufacture of fertilizers, soda, dynamite, and kerosene oil, millions of pounds are used annually. Its use is of such importance that some one is said to have remarked that “the advance of a nation in civilization might be well measured by the amount of sulphuric acid which it uses annually.”

**Nordhausen Sulphuric Acid.** — Nordhausen sulphuric acid differs from ordinary sulphuric acid in containing sulphur trioxide or sulphuric anhydride held in solution by the normal acid. It is represented by the formula  $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$  or  $\text{H}_2\text{S}_2\text{O}_7$ . It is prepared by distilling ferrous sulphate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ). This compound is partially dried before it is distilled. The reactions that take place are represented thus : —



The compound is also made by dissolving sulphur trioxide in ordinary sulphuric acid.

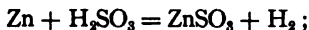
Commercial Nordhausen sulphuric acid is an oily, fuming, and heavy liquid having a specific gravity of 1.9. When it is pure, it is a solid crystalline substance which melts at  $35^\circ$ . It unites with water and forms ordinary sulphuric acid. The acid forms stable salts with many bases. With sodium and potassium the salts are, respectively,  $\text{Na}_2\text{S}_2\text{O}_7$  and  $\text{K}_2\text{S}_2\text{O}_7$ .

The acid was named Nordhausen sulphuric acid from the name of a town in Saxony where it is prepared for the market. It is also called disulphuric acid and pyrosulphuric acid. The latter name, *pyrosulphuric acid*, is given to it to indicate that it

is produced by heating a sulphate, the prefix *pyro* signifying heat.

*Other Oxides and Acids of Sulphur.*

**Hyposulphurous Acid and its Salts.**—When sulphurous acid is treated with zinc, hydrogen is not set free, according to the reaction



but the following reaction does occur :—



This reaction probably occurs in two steps ; that is, in the first change zinc sulphite and hydrogen are formed, but the nascent hydrogen attacks the sulphurous acid and removes a molecule of water, one molecule of the acid yielding one molecule of hyposulphurous acid and one molecule of water.

The compound is very unstable, changing rapidly to sulphur dioxide, free sulphur, and water. The acid itself has not been isolated ; but when sodium acid sulphite in solution is treated with zinc, a sodium salt ( $\text{NaHSO}_2$ ) is produced along with other products. When brought in contact with oxygen or substances yielding oxygen, it becomes first sulphurous acid and finally sulphuric. It acts much more powerfully in removing oxygen from compound than does sulphurous acid. The only salts of this acid are those of potassium and sodium ; that is, the only salts that have been separated from their water solution. The water solution of the pure acid is obtained from these salts. These salts rapidly become sulphites when exposed to the air. The acid is monobasic.

The anhydride of this acid sulphur monoxide ( $\text{SO}$ ) is not known.

Disulphur trioxide ( $\text{S}_2\text{O}_3$ ) and disulphur heptoxide ( $\text{S}_2\text{O}_7$ )

have been known for a long time. They are very unstable bodies, being broken up when the conditions under which they are formed are removed. They do not react with water to form corresponding acids, but break up, forming sulphuric acid, sulphur dioxide, and sulphur in case of the trioxide, and sulphuric acid and oxygen in case of the heptoxide.

**Thiosulphuric Acid and its Salts. — Preparation.** — Thiosulphuric acid has not been isolated, its salts only being known. To 20 g. of sodium sulphite in a solution of water add flowers of sulphur, and boil as long as sulphur dissolves, say from twenty to thirty minutes. (The water solution of the sulphite should be made in previously boiled water. Why? The solution should be nearly saturated.) Allow the excess of sulphur to settle out, and pour off the clear solution. Place this solution in a crystallizing dish, and let it stand until the salt crystallizes out. The compound formed has been determined to have the formula  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , and is called sodium thiosulphate, or commercially it is known as hyposulphite of sodium. The reaction may be represented thus: —



How does this compare with the union of oxygen and sodium sulphite? Compare it with the sulphate.

**Experimental Study, No. 43.** — (a) Dissolve a crystal of the salt prepared as just directed in water, and treat with dilute hydrochloric acid. What is the white precipitate? Add the hydrochloric acid as long as the precipitate is formed, and allow the precipitate to settle out, and test the liquid for sulphites. (See under SULPHITES.) Test some of the original solution in the same way. Also test a solution of a known sulphite, adding hydrochloric acid.

(b) To 10 cc. of a solution of the sodium salt add a few drops of sulphuric acid. What is the precipitate? What gas escapes? What is its source? What effect will the sulphuric



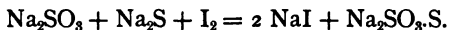
acid have on the base sodium; that is, in reference to its combination?

(c) Treat 10 cc. of a solution of silver nitrate with a solution of sodium chloride as long as any precipitate is formed. What is the precipitate? Allow the precipitate to settle, decant off the water, and add a solution of sodium thiosulphate, and note the result.

(d) To a solution of chlorine gas add a solution of sodium thiosulphate in excess. Examine the solution for chlorine; that is, free chlorine. What has become of the chlorine? Test the solution for a sulphate. Explain the result.

**Properties of Thiosulphuric Acid and its Salts.** — It has been seen that the sulphites readily take up an atom of oxygen, becoming sulphates. Sulphur enters the molecule in much the same way, requiring, however, a higher temperature to produce the change. This compound may therefore be regarded as a sulphate of sodium in which one of the atoms of oxygen is replaced by sulphur.

There are several other methods for the preparation of the sodium or potassium salts of this acid. For example: when sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), sodium sulphide ( $\text{Na}_2\text{S}$ ), and iodine are warmed together in solution, the iodine unites with the sodium of the sulphide, and the nascent sulphur enters the molecule of sodium sulphite. The reaction is represented thus: —



The acid corresponding to the salt has not been formed. When, for example, sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) is treated with sulphuric acid (in fact, with almost any acid), the sodium is removed from the molecule, and sodium sulphate is formed; but the hydrogen does not take the place of the sodium, thus forming thiosulphuric acid, but the compound is immediately broken up, and water, sulphur dioxide, and free sulphur are formed.



The reaction of sulphuric acid with the salts of this acid is as follows : —

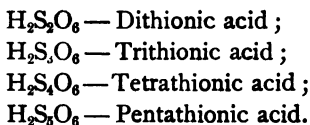


This reaction affords a ready means of distinguishing sulphites from thiosulphates, since both yield sulphur dioxide ( $\text{SO}_2$ ) with sulphuric acid ; but the solution containing the sulphite remains clear, while the solution containing the thiosulphate becomes turbid because of the sulphur which is set free.

Sodium thiosulphate is the principal salt of this acid, and is used quite largely as an antichlor in paper manufacture, as a solvent for the unchanged silver salts in photography, and as a reagent in the chemical laboratory. (For the latter, see under the study of SILVER.) As an antichlor it changes the chlorine to hydrochloric acid, furnishing oxygen to the thiosulphate, which becomes a sulphate.

The *thio* of the name *thiosulphuric* is derived from the Greek word for sulphur, and therefore literally means *sulphur*, or *sulpho*, sulphuric acid.

Four other acids (or their salts) of sulphur are known and have been prepared. They are of interest, however, purely from the chemical standpoint. They are represented by the following formulæ : —



*Compounds of Selenium and Tellurium with Oxygen, and with Oxygen and Hydrogen.*

Selenium and tellurium are rare elements, and their compounds are therefore of but little general interest. They

resemble sulphur in their properties and in the compounds which they form. Both elements form oxides, and these oxides, when brought in contact with water, form acids. The valence of these elements varies from 2 to 6. The oxides, therefore, will have the formulæ  $\text{SeO}(\text{?})$ ,  $\text{SeO}_2$ ,  $\text{SeO}_3$ ,  $\text{TeO}(\text{?})$ ,  $\text{TeO}_2$ , and  $\text{TeO}_3$ . The trioxide of selenium has not been prepared, but its acid has been made. The acids produced by the action of water on the oxides are  $\text{H}_2\text{SeO}_3$ ,  $\text{H}_2\text{SeO}_4$ ,  $\text{H}_2\text{TeO}_3$ , and  $\text{H}_2\text{TeO}_4$ , corresponding to sulphurous and sulphuric acid.

These acids are dibasic and form two series of salts ; that is, the acid and the normal salts.

These elements have less affinity for oxygen than does sulphur. The lower oxides and acids do not readily take oxygen to become the higher oxides and acids.

### *Compounds of Nitrogen with Oxygen and with Oxygen and Hydrogen.*

**Oxides of Nitrogen.** — It has been previously shown that nitrogen does not unite with any of the elements under ordinary conditions. Its greatest affinity is for hydrogen, forming the compound ammonia ( $\text{NH}_3$ ).

The oxides of nitrogen do not exist free in nature, but are formed from compounds known as nitrates, which are found in the soil and in many other places in large quantities. (See under NITRIC ACID AND NITRATES.)

### NITROUS OXIDE OR NITROGEN MONOXIDE.

**Methods of Preparation.** — When electric sparks are passed for a long time through dry air, a red-colored gas is produced, which is found to be nitrogen peroxide ( $\text{NO}_2$ ). If water is present, nitric acid is formed, which unites with ammonia, which is formed at the same time, producing ammonium nitrate

( $\text{NH}_4\text{NO}_3$ ), from which nitrate the oxide of nitrogen under consideration can be formed. In order to prepare the gas absolutely pure, it should be passed through a solution of potassium hydroxide, and then through a solution of ferrous sulphate. The potassium hydroxide removes any chlorine or any free acids that may come from impurities found in the ordinary ammonium nitrate, and ferrous sulphate removes the other oxides of nitrogen that may be formed at the same time.

**Preparation.** — Place in a 100 cc. flask or a large test-tube 15 g. of dry ammonium nitrate and prepare the apparatus for collecting gas over hot water (30 to 50°). Heat gently until the substance fuses (about 230°) and the gas begins to escape freely, then heat only sufficiently to keep up the flow of gas. Collect a sufficient number of bottles of gas for further study.

**Experimental Study, No. 44.** — (a) Prove the relative mass of the gas to air by inverting a bottle of the gas over a bottle of air and allowing it to stand for two minutes. Test each bottle with a burning stick. (See *d*.)

(b) Transfer one-half a bottle of gas to another bottle by allowing the gas to displace the water; close the bottle with the hand, or with a solid rubber stopper, and shake vigorously. (The water should be cold.) Open the bottle with the mouth under water. Note the facts. This may be repeated several times. The gas must be free from air.

(c) Study the gas for its other physical properties, odor, taste, etc.

(d) Test bottles of the gas with a burning stick, with phosphorus, sulphur, carbon, with magnesium, both at high and low temperatures. Cover the bottles after each reaction and examine the products with litmus, and compare them with those produced by these elements and oxygen. (See study of OXYGEN.) Explain these changes.

(e) Test the gas with moistened litmus paper, also the water in which the gas is dissolved.

(*f*) Place the pure gas in a eudiometer tube over mercury, and pass electric sparks as long as the volume of the gas in the eudiometer tube increases. Compare the new volume with the original volume. Bring the gas in contact with potassium pyrogallate. Note the volume of the remaining gas and prove what it is.

(*g*) Mix in the eudiometer tube equal volumes of the gas and hydrogen, and pass the electric spark. Examine the volume of the product and the gas remaining. What is the latter? The compound with hydrogen will be what? How much oxygen is there in the gas; that is, by volume as shown by this result?

(*h*) The gas may be analyzed by filling a tube like Fig. 10 about half full of the gas over mercury. Pass into the tube a piece of potassium about as large as a pea; the potassium should be free from naphtha and as free from the oxide as is possible. The potassium must be placed at the end (*a*) of the tube, and warmed until the action takes place. Cool, and examine the gas left in reference to its volume and what it is.

(*i*) Show that water is one of the products of the decomposition of the ammonium nitrate by passing the decomposed products through a cold vessel. This is done by inserting between the generator and the collecting bottle a small bottle, and keeping this bottle cold by surrounding it with cold water.

(*j*) Carefully heat a piece of ammonium nitrate half as large as a pea on a piece of platinum foil. Notice what becomes of the nitrate.

**Physical Properties.** — Nitrogen monoxide is a colorless and odorless gas having a sweet taste. It is soluble in cold water, which at  $0^{\circ}$  dissolves a little more than 1 vol. of gas to every volume of water. It has been converted into a solid at  $-115^{\circ}$ . It is a liquid at  $0^{\circ}$  under a pressure of 450 pounds. If this liquid is exposed to a vacuum, it is rapidly converted into the gas, producing a temperature of  $-140^{\circ}$ . Its vapor density

is 21.98. At red heat the gas is decomposed into nitrogen and oxygen.

**Chemical Properties.** — When a glowing hot stick is placed in a bottle of the gas, chemical action is greatly increased, much as it would be if it were placed in pure oxygen. At ordinary temperatures it does not give up its oxygen to phosphorus, carbon, magnesium, potassium, and similar substances, but at higher temperatures, about red heat, the action resembles that produced when these substances are placed in pure oxygen.

The electric spark decomposes it into nitrogen and oxygen, 2 vols. of the gas yielding 2 vols. of nitrogen and 1 vol. of oxygen. When the oxygen is removed from it by hydrogen or potassium, there remains 1 vol. of pure nitrogen gas for each volume of the gas taken.

**Calculation of Formula.** — The compound has been shown to consist of oxygen and nitrogen, and that for every 2 vols. of the gas there are 2 vols. of nitrogen and 1 vol. of oxygen. What will 2 l. of the gas weigh under standard conditions, the density being 21.98? How much by mass is the oxygen, and how much is the nitrogen?

From the facts known, show that the formula for the molecule is  $N_2O$ . These facts are : —

- (a) Those of percentage composition ;
- (b) The density of the gas, and therefore molecular mass ;
- (c) Atomic mass of the elements composing the molecule ;
- (d) Volumetric composition.

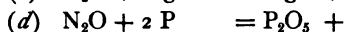
**Name and History.** — This compound is known as nitrogen monoxide, nitrous oxide, or nitrogen protoxide (*proto*, first or lowest). It is also called “laughing” gas. Nitrogen monoxide was discovered by Priestley in 1772. It was prepared by him by the action of sulphites on nitric oxide (NO), the sulphite becoming a sulphate.

**Uses.** — The pure gas when inhaled produces an anæsthetic

effect. When it is mixed with air it produces in many persons excitement and feeling of exhilaration. The effects are of short duration, and, if the gas is pure, are harmless. If, however, it is inhaled for a long time, it produces suffocation. It is used in surgical operations that require but a short time for their completion, and especially in dental surgery.

It is now furnished to dentists in the form of a liquid contained in strong vessels. The liquid is converted into a gas by opening a stop-cock, thus relieving the pressure, when a portion of the liquid escapes as a gas.

#### REACTIONS.



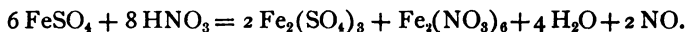
Explain and balance each of the equations and read the reaction gravimetrically and volumetrically. What effect has the heat in reaction (a)? Can the compound be made from the elements?

How much ammonium nitrate would be required to prepare 10 l. of nitrogen monoxide?

#### NITRIC OXIDE.

**Methods of Preparation.** — When nitric acid acts on most metals, it is decomposed, and a gas is produced along with nitrates of these metals and water. To obtain the gas free from impurities, it is passed into a cold concentrated solution of ferrous sulphate ( $\text{FeSO}_4$ ). The gas is then driven off from this solution by heat, and collected over water. The pure gas is easily prepared by the action of concentrated nitric acid on

ferrous sulphate. Concentrated acid is added to the solid salt and heated. The reaction is :



**Preparation.** — 25 g. of copper filings or turnings are placed in a 100 cc. flask prepared for collecting gas over water. Pour down a thistle-tube sufficient concentrated nitric acid to cover the copper. The reaction goes on without applying heat. Collect sufficient amount of the gas for its study. Add more acid as may be required. The temperature must not be high, since nitrogen monoxide is formed under these conditions.

**Experimental Study, No. 45.** — (a) Examine for physical properties.

(b) Pass into a bottle partly filled with the gas, air or (better) pure oxygen. Note the effect on the volume of the gas, etc. The compound is chiefly nitrogen dioxide ( $\text{NO}_2$ ). Note that this fact is used in preparing sulphuric acid. How? Why?

(c) Test the gas in the same way that nitrogen monoxide was tested ; that is, with magnesium, phosphorus, and sulphur. Note the effect of temperature on the decomposition : *e.g.* bring sulphur or phosphorus in contact with the gas before it is rapidly oxidizing, and also after it is rapidly oxidizing. Explain why the action begins in one case and does not in the other.

(d) Stopper a bottle of the gas while the mouth is held under water. Remove it carefully from the trough, and add a few drops of carbon disulphide ( $\text{CS}_2$ ). Close the bottle again, and shake well. Next open, and bring a burning stick near the mouth of the bottle. Cover the bottle, and examine the products with the nose, etc., to determine what they are.

(e) Determine the volumetric composition of the gas by potassium, exactly as described under carbon monoxide.

(f) To a measured volume of nitric oxide add pure oxygen as long as any gas remains, and determine the volume of oxy-



gen used. If carefully manipulated, just enough oxygen can be used to combine with the nitric oxide. The product is absorbed by the water as fast as it is produced. An excess of oxygen may be admitted, and the amount used determined by difference. Note the volume of oxygen used as compared with that of the nitric oxide.

(g) Pass the gas into a solution of ferrous sulphate, or add to a bottle of gas 100 cc. of such a solution; close the bottle, and shake. Note the effects of the ferrous sulphate solution. Remove the stopper of the bottle when the mouth is held under water. The compound formed is said to have the formula  $2 \text{FeSO}_4 \cdot \text{NO}$  or  $\text{FeSO}_4 \cdot 2 \text{NO}$ .

**Physical Properties.** — Nitric oxide is a gas, slightly heavier than air, its density being 14.98. It is also a colorless, condensible gas. It is not readily decomposed by heat or by chemical means, and is the most stable of the oxides of nitrogen. The gas is but slightly soluble in water.

**Chemical Properties.** — The most marked chemical property of nitric oxide is shown by its action with oxygen. The product of this action is a brown gas, which is largely nitrogen dioxide ( $\text{NO}_2$ ). This reaction serves to distinguish this gas from other colorless gases. It does not give up its oxygen as readily as does nitrous oxide ( $\text{N}_2\text{O}$ ). However, phosphorus, potassium, and sodium at high temperatures do decompose it, setting nitrogen free and forming the oxides of the elements mentioned.

When heated with potassium, a given volume of the gas (say 1 l.) yields  $\frac{1}{2}$  l. of nitrogen. When in contact with pure oxygen, 2 vols. of nitric oxide unite with 1 vol. of oxygen to form 2 vols. of nitrogen dioxide ( $\text{NO}_2$ ). When the gas comes in contact with ferrous sulphate, a compound is formed having a dark brown color, represented by the formula  $2 \text{FeSO}_4 \cdot \text{NO}$  or  $\text{FeSO}_4 \cdot 2 \text{NO}$ . This is a characteristic reaction.

When the gas is mixed with carbon disulphide ( $\text{CS}_2$ ), and

the temperature of any portion of it is raised to red heat, the action continues, producing a bright, luminous flame, rich in actinic rays. The principal use of the gas is in the preparation of sulphuric acid.

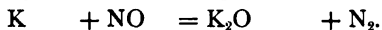
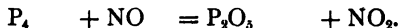
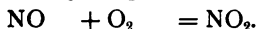
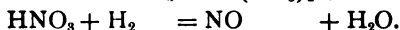
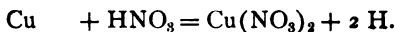
**Determination of Formula.** — Show from the following facts that the formula of the molecule of nitric oxide is NO.

(a) Weight of 1 l. of the gas is known, and the volume of oxygen and nitrogen in a given volume of the compound. From these facts the per cent of oxygen and nitrogen can be determined. Determine these per cents.

(b) The vapor density of the gas is 14.98.

(c) The atomic mass of the elements hydrogen and oxygen is known.

#### REACTIONS.



Balance and explain each of the above equations, and read by quantity and by volume ; that is, when the molecules are gaseous.

**Problem.** — How much carbon disulphide by volume and by mass is required to react with 5 l. of nitric oxide ?

#### *Nitric Dioxide and Nitrogen Tetroxide.*

It has just been pointed out that 2 vols. of nitric oxide unite with 1 vol. of oxygen, forming 2 vols. of the compound, which can be shown to have the formula  $\text{NO}_2$ . It can be prepared by heating dried nitrates, like lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), until decomposition takes place. Lead oxide ( $\text{PbO}$ ), nitrogen dioxide, and oxygen are the products. (Write the reaction.)

It is a dark brown gas quite easily condensible to a liquid. It readily yields its oxygen to elements or compounds that readily take it up, as has been shown in case of sulphur dioxide ( $\text{SO}_2$ ). Its density varies with the temperature to which it is subjected within certain limits. At  $150^\circ$  the vapor density is 23, corresponding to the formula  $\text{NO}_2$ . (Explain how.) If cooled down to about  $25^\circ$ , its density corresponds to the molecule  $\text{N}_2\text{O}_4$ . It is probable, therefore, that dissociation is complete at about  $150^\circ$ , and that between this temperature and  $25^\circ$ , the gas is a mixture of the compounds  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ . (See explanation under VALENCE OF NITROGEN.)

When water is added to the gas, the solution becomes acid. If the water is cold, there is a mixture of two acids, nitrous and nitric. (See below for tests of these acids.) If the water is hot, only one acid, nitric acid, is formed. Nitric oxide is also present.

#### NITROGEN TRIOXIDE.

**Methods of Preparation.**—This oxide is formed when a small volume of oxygen is added to a large volume of nitric oxide, usually 4 vols. of nitric oxide ( $\text{NO}$ ) to 1 vol. of oxygen. It is also prepared by treating a nitrite, like sodium nitrite, with dilute acids. The most common method for its production is by the action of arsenious oxide ( $\text{As}_2\text{O}_3$ ) with nitric acid of specific gravity 1.3 (48 per cent acid).

**Preparation, and Experimental Study, No. 46.**—(a) Place 5 g. of arsenious oxide ( $\text{As}_2\text{O}_3$ ) in a 100 cc. flask, and add nitric acid, specific gravity 1.42, diluted with half its volume of water. Heat gently and pass the gas into 100 cc. of ice cold water (best previously boiled for five or ten minutes). Examine the water with litmus, and when diluted, by tasting.

(b) Pass the gas into a dilute solution of potassium hydroxide until the solution is slightly acid. Retain this solution and

solution (a) for further examination. (See under NITROUS and NITRIC ACIDS.)

(c) Pass the gas through a tube (sulphur dioxide tube) surrounded by a freezing mixture. Examine the product and describe.

**Properties of Nitrogen Trioxide.** — Nitrogen trioxide is condensed to a blue liquid at temperatures not far from  $0^{\circ}$ . It is easily decomposed into nitrogen tetroxide ( $N_2O_4$ ) and nitric oxide. Its density is not certainly known, but it is probably 37.95. From this density and its method of formation from nitric oxide, the formula is given as  $N_2O_3$ . For example, 4 vols. of nitric oxide unite with 1 vol. of oxygen to form 2 vols. of nitrogen trioxide. It unites with water to form an acid known as nitrous acid ( $HNO_2$ , or  $H-O-NO$ ). The oxide is also called the anhydride of nitrous acid.

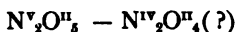
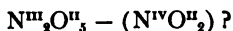
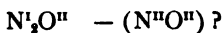
#### NITROGEN PENTOXIDE.

This compound is prepared from nitric acid by removing the water from it by means of phosphorus pentoxide, owing to the great affinity of the latter for water. To the pure anhydrous acid is added phosphorus pentoxide ( $P_2O_5$ ) in the proportion of 63 parts of the acid to 71 parts of the oxide. The temperature must be kept at or below  $0^{\circ}$ . When the oxide is brought in contact with water, an acid solution is formed containing nitric acid.

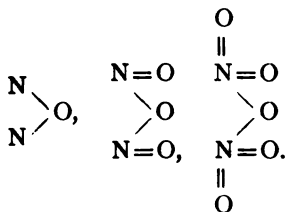
**Properties.** — Nitrogen pentoxide is a crystalline solid changed to a liquid when heated carefully to about  $30^{\circ}$ . It is very unstable, and spontaneously decomposes, often explosively so. It is of interest only because of its connection with nitric acid. The formula for this oxide is  $N_2O_5$ .

**Valence of Nitrogen.** — It has been already established that nitrogen is a triad in reference to hydrogen. An examination of the formulæ for the oxides shows that if oxygen be con-

sidered a fixed dyad, then nitrogen has a variable valence. The following are the oxides : —

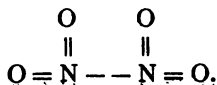


In the first series of oxides the valence of nitrogen is regarded as unity, 3 and 5. According to this idea they may be represented in the order mentioned, thus : —



This variability of valence agrees with the general statement that when the valence of an element varies in any degree, it increases or decreases by twos. The second series at first thought appears to disprove this statement. The valence appears to be 2 and 4.

It will be remembered that nitric oxide always takes up more oxygen, under proper conditions, and becomes nitrogen dioxide ( $\text{NO}_2$ ), or  $2 \text{NO}_2 = \text{N}_2\text{O}_4$ . If the tetroxide is heated, its density decreases until it corresponds to a gas with a molecular formula  $\text{NO}_2$ ; that is, to a gas whose formula is one-half that of the original substance. If nitrogen is considered pentivalent in nitrogen dioxide, then the tetroxide could be accounted for by the following structure : —



This represents the valence of nitrogen as 5, and that the compound is made up of two molecules,  $\text{NO}_2$ . These molecules are held together by a unit of valence that entirely disappears on heating the compound. One fact is established in reference to the property of valence, and that is that it may be entirely destroyed by heat. We might speak of this as a remnant of valence not sufficient to hold another atom of oxygen, but readily active with a like remnant of a compound or group of atoms.

In considering this question we should keep in mind the conception of valence as a mutual property of two or more elements.

#### *Action of Water on the Oxides of Nitrogen.*

As has been seen, the three oxides,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_5$ , each form an acid by the taking up of water. Unfortunately these acid compounds are with difficulty separated from the water with which they are mixed; in fact, only the latter, nitric acid, can be so separated. Our knowledge of the existence of these acids depends on our knowledge of the compounds which they form with bases.

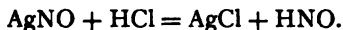
These reactions may be represented by the following:—



The other oxides do not have acids corresponding to them, but form one or more of the acids just given in contact with water. These acids are named according to the system of nomenclature, hyponitrous, nitrous, and nitric acid, in the order written.

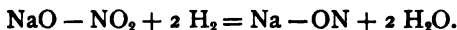
**Hyponitrous Acid.**—This acid is not actually formed by adding water to nitrous oxide ( $\text{N}_2\text{O}$ ), although the oxide may

be regarded as the anhydride of the acid. It can be produced in solution by treating its salts, like silver hyponitrite ( $\text{AgNO}$ , or  $\text{Ag}_2\text{N}_2\text{O}_2$ ), with dilute hydrochloric acid. In this case the silver unites with chlorine, forming silver chloride ( $\text{AgCl}$ ), and the hydrogen of the acid takes the place of the silver : —



It can be prepared from sodium nitrate, or nitrite, by treating it in solution with nascent hydrogen, the hydrogen being produced from sodium amalgam. What is the action of hydrogen on oxygen? Why not produce the hydrogen from zinc and sulphuric acid?

#### REACTION.



### NITRIC ACID AND NITRATES.

**Occurrence and Method of Production in Nature.** — It has been shown that oxygen and nitrogen do not unite under ordinary conditions. It will be noticed that all these oxides of nitrogen studied have been really prepared from more complex compounds; that is, from nitric acid ( $\text{HNO}_3$ ) or from nitrates. Hence the question arises, How are these compounds produced? This is a question of great practical importance. All animal and vegetable bodies contain combined nitrogen, and of course this element must be supplied in the food of these organisms, either as a free element, — *e.g.* as oxygen is largely supplied to animals, — or as combined nitrogen. We also know that nitrogen constitutes about four-fifths of the atmosphere in which these organisms live. We know further that animal organisms do not obtain their nitrogen from the element in the atmos-

phere, but from plants that form a part of their food. Whence do the plants, therefore, get their nitrogen? It is still a doubtful question whether plants obtain any of their nitrogen directly from the air. Plants can absorb ammonia to a certain extent, but only a very small amount of nitrogen is obtained from this source. We might start from a condition when all the nitrogen of the earth was in its atmosphere, or combined in animal and vegetable matter. This would bring us to the following experiments and facts of observation. If, for example, any animal substance, such as the hair, nails, etc., be heated away from the air, the compounds forming the substance are broken up, and among the products ammonia is always found. The same substance is easily recognized as arising from the decaying manure of a stable. Here it is produced by the decomposition of the animal excrement. These latter changes are sometimes said to be spontaneous, but investigation shows that the cause is to be found in minute organisms, which find a place for growth and development where these nitrogenous substances are. Now when ammonia is in the soil, under proper conditions, it undergoes oxidation either to nitric or nitrous acids, and if bases are present like potassium, sodium, or ammonium, corresponding salts are formed. This is illustrated by the method used for producing saltpetre. Refuse organic matter is mixed with wood ashes (which contain potassium) and covered with earth, loosely, so that air can have free access. These masses of matter are protected from rains by open sheds. In course of time potassium nitrate appears in the heap. There are many places on the earth where nature furnishes all the conditions for these reactions, so that large quantities of this salt or the sodium salt are produced; for example, in India potassium nitrate is found as an incrustation on the soil. In the dry region on the west coast of South America sodium nitrate is found in immense quantities, which undoubtedly had its origin in a manner similar to that just described; *i.e.* in a dry atmosphere and in presence of decaying



organic matter. On the coast of Chili it is dug in large quantities and shipped to Europe and North America. This process of producing nitrates in the soil is called nitrification, and takes place best in warm dry climates, other things being equal. The cause is minute organisms, called bacteria, which seem to act as carriers of oxygen. The compounds produced are soluble, and in this condition are furnished to the plants which build the nitrogen into the compounds that form an essential part of their structures. These vegetables are decomposed in course of time, and their nitrogen passes through the same cycle of changes once more. Again, the plant may be used as a food for an animal, and its nitrogen become a part of the matter of the animal body. Sooner or later it leaves the animal body, or the animal dies, and its final nitrogen supply becomes largely ammonia, and the cycle of changes is thus complete.

These compounds — that is, ammonia and the nitrates — are the sources of all the inorganic compounds of nitrogen. Small amounts of nitric acid are produced in the atmosphere by means of electric discharges. It is probably true that certain organisms have the power of directly fixing the nitrogen of the air.

**Preparation.** — Place in a 150 cc. retort or flask 20 g. of potassium nitrate and cover it with concentrated sulphuric acid. Join the generator and the receiver, placing the latter so that it can be kept cool by running water, or by floating it in the water trough. Heat slowly, until a sufficient quantity of the distillate has been collected, usually about 50 cc.

**Experimental Study, No. 47.** — (a) Examine and note physical properties.

(b) Dilute 1 cc. of the solution with 10 cc. of water and test it with litmus paper; also test the concentrated solution of the acid in the same way.

(c) Neutralize 20 cc. of potassium hydroxide solution with the acid and evaporate it to dryness. Redissolve the solid

residue in the least possible amount of water and allow the compound to crystallize out. Examine the compound. What is it? Compare with the original substances.

(*d*) Proceed in the same manner as in (*c*), using ammonium hydroxide in place of the potassium hydroxide. Compare the salts of (*c*) and (*d*) with samples of potassium and ammonium nitrate.

(*e*) Treat a small piece of tin with 10 to 15 cc. of acid, and heat. What becomes of the tin? What gas escapes? The white compound formed is stannic oxide ( $\text{SnO}_2$ ).

(*f*) Dip into the concentrated solution of the acid a piece of copper foil. What gas escapes? To what is the color due? Notice the color of the solution.

(*g*) Dip, for two seconds, a piece of white silk into the acid and note the effect. Expose the silk afterwards to acid for a longer period. Rinse the silk well and dip in a dilute solution of ammonium hydroxide.

(*h*) Heat a piece of charcoal nearly red-hot and drop it into 10 cc. of fuming nitric acid held in a 100 cc. beaker. Keep the beaker covered and explain what occurs.

(*i*) Add a few drops of the acid to 10 cc. of a solution of ferrous sulphate. Heat and examine the escaping gas. What is it? Compare with the result produced by nitric oxide and ferrous sulphate.

(*j*) Fuse in a deflagrating-spoon some potassium nitrate and drop into it an intimate mixture of charcoal and sulphur which has been thoroughly dried. They should be mixed in about equal volumes. Explain what occurs. Notice the odor of the products. What are they? Treat the residue with a few drops of hydrochloric acid, and note the result.

(*k*) Heat a small piece of potassium nitrate on charcoal by means of a blow-pipe or by the lamp flame. Explain the result.

(*l*) Produce hydrogen from powdered zinc and potassium

hydroxide and add a solution of a nitrate. Heat, and examine the escaping gas for ammonia. Would hydrogen from zinc and sulphuric acid produce the same result? If not, why?

**Physical Properties.** — Nitric acid is a volatile, colorless liquid. It is, however, usually colored yellowish brown from the oxide of nitrogen that is dissolved in it. It is decomposed by heat and by sunlight, the main products being water, oxygen, and nitrogen dioxide. Its vapor density has not been actually determined, owing to the ease with which it is decomposed, but it is probably 31.5. The pure acid gives off fumes when exposed to the air. The ordinary nitric acid of commerce contains 30 or more per cent of water. The water may be removed, however, by distillation with concentrated sulphuric acid, when the sulphuric acid retains a large part of the water. The acid mixes with water in all proportions, the mixing being accompanied by a rise in the temperature of the solution. The solution of pure acid begins to boil at  $86^{\circ}$ , but the temperature gradually rises until it reaches about  $120.5^{\circ}$ , when it becomes constant and a distillate passes over which has a specific gravity of 1.41, and contains 68 per cent of acid. If this distillate is distilled from a mixture with pure sulphuric acid, nearly all of the water can be removed, and a volatile liquid containing 99.5 per cent of acid passes over.

**Chemical Properties.** — Nitric acid acts readily upon litmus paper; and if the acid is concentrated, it destroys it. It destroys organic matter, such as skin, nails, etc., by its decomposition, from which oxygen is supplied to the organic matter. If the acid is dilute, it colors most animal substances yellow, as is seen in dyeing silk and wool.

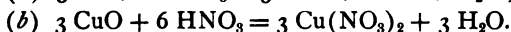
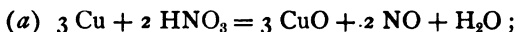
It neutralizes definite quantities of bases, forming salts, such as potassium and sodium nitrates. It is found that 63 parts of nitric acid neutralizes 56 parts of potassium hydroxide or 40 parts of sodium hydroxide.

Its most characteristic chemical property is shown by its action on the metals such as tin and copper. In general, it may be said that it forms oxides with all the metals excepting gold and platinum. The products are mostly nitric oxide and water. In most cases (antimony, arsenic, and tin being exceptions) it acts at the same time on the oxides, forming nitrates and water. Two molecules of the acid always yield one molecule of water, two molecules of nitric oxide, and three atoms of oxygen. (See under Preparation of Nitric Oxide for the Reaction with Copper.) With tin the reaction is thus : —



One atom of tin requires two atoms of oxygen, but two molecules of the acid yield three atoms of the oxygen ; hence, in order that all the atoms shall enter into combination, it will require four molecules of nitric acid and three atoms of tin to complete the reaction.

The reaction with copper may be taken as representing its action on most other metals. The action is here repeated, and considered as divided into two parts : —

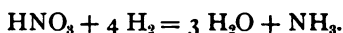


In (a) the two molecules of acid give up three atoms of oxygen ; and since copper is a dyad, three molecules of copper oxide are formed. The equation (b) represents the action of more acid on the oxide of copper, forming the nitrate. Of course there is no such visible division in the action. The copper oxide is insoluble in water, but the copper nitrate is soluble ; and as fast as the molecules of the oxide are formed, they are converted into the nitrate and dissolved.

In case of tin, however, the reaction did stop with the formation of the oxide, the nitrate not being formed in this way. (In what condition is the oxygen in this reaction? Compare

the action of the oxygen of the air on copper and on tin with this action.)

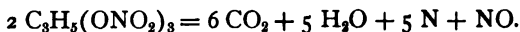
With ferrous sulphate in solution, nitric acid produces a brown to black compound. The result is the production of the compound  $\text{NO} \cdot 2\text{FeSO}_4$ . (See NITRIC OXIDE.) The iron is oxidized from ferrous oxide ( $\text{FeO}$ ) to ferric oxide ( $\text{Fe}_2\text{O}_3$ ), and nitric oxide is thus set free, which reacts with a portion of the unchanged ferrous sulphate. Carbon is rapidly oxidized by concentrated nitric acid. Nascent hydrogen removes the oxygen from nitric acid and its salts, producing ammonia as a final change. The final reaction is written thus : —



Salts of this acid yield their oxygen to other substances, but not at ordinary temperatures. For example, when potassium nitrate is heated with carbon and sulphur, the oxides of the two elements are formed. This fact is the basis for the formation of gunpowder, which is an intimate mixture of sulphur, carbon, and potassium nitrate. When the temperature of any part of this mixture is raised to red heat, the action begins, and continues until the change is complete. The products are largely gaseous (what are they?), and under the influence of the heat of the reaction exert great expansive force. (See GUNPOWDER.)

**Uses of Nitric Acid.** — Nitric acid is a necessary agent in the chemical laboratory and in a large number of manufacturing processes. All of the most commonly used explosives depend in some way upon nitric acid for their useful properties. Such substances as nitro-glycerine, guncotton, dynamite, gunpowder, etc., are examples. The general character of these compounds may be discovered by an examination of nitro-glycerine. It is represented by the formula  $\text{C}_3\text{H}_5(\text{ONO}_2)_3$ . This molecule is very unstable, and when decomposed the oxygen unites with the carbon and hydrogen, producing gas-

eous products. The decomposition is accompanied by much heat, thus causing a great expansion in the gases produced. The decomposition may be represented thus : —



It will be noticed that all these products are gaseous, and that the formation of the products, carbon dioxide and water, produces a large amount of heat, — 68,000 calories for the water, and 96,960 calories for the carbon dioxide.

Nitric acid is also required in the manufacture of sulphuric acid, in making nitrates, and in the preparation of the aniline dyes.

**Formula for Nitric Acid.** — The formula for this acid cannot be determined by the use of the vapor density method, since its density has not been accurately determined. However, the supposed vapor density and the facts of analogy give a formula for the acid that agrees with all other known facts.

An analysis of the acid shows that it is composed of 1.58 per cent of hydrogen, 22.23 per cent of nitrogen, and 76.19 per cent of oxygen. Since the acid forms but one class of salts, and no salt contains hydrogen, it is considered to have but one atom of hydrogen. It has also been pointed out that 63 parts of acid react with 56 parts of potassium hydroxide and 40 parts of sodium hydroxide. Now 40 parts of sodium hydroxide contain 23 parts of sodium, and 56 parts of potassium hydroxide contain 39 parts of potassium. These correspond to an atom of each element. Taking hydrogen as unity, there are 14.01 parts of nitrogen and 47.88 parts of oxygen. The atomic mass of the elements being known, the formula might be  $\text{HNO}_3$ . The same proportions would be observed if the formula should be represented by  $\text{H}_2\text{N}_2\text{O}_6$  or  $\text{H}_2\text{N}_3\text{O}_9$ , etc. It has been shown that one atom of hydrogen exchanges with one atom of potassium; that is, that potassium is a monad. Now if there are two or more atoms of hydrogen in a molecule

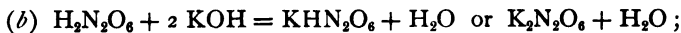
of nitric acid, it should be possible to replace the atoms of hydrogen, one at a time, by potassium, according to the method shown in the study of sulphuric acid. No salt of nitric acid and potassium contains hydrogen, and the amount of potassium is the same under all conditions. The formula is therefore  $\text{HNO}_3$ .

**Experimental Study, No. 48.** — The facts stated in the preceding paragraph may be shown experimentally, as follows : Place in each of two weighed porcelain evaporating dishes 20 cc. of a solution of potassium hydroxide (or exactly the same mass of this solution in each dish). Neutralize exactly the alkali in each dish, taking note of the amount of nitric acid used. Now run into one of the dishes just as much more nitric acid. Evaporate the contents of each dish to dryness, being careful that there is no loss of solid material by a too rapid evaporation. (This evaporation should be done on a water bath.) When thoroughly dry, weigh the two dishes, and determine the amount of solid material in each. If the extra nitric acid does not enter into combination, what becomes of it? It will be found that there is exactly the same amount of salt in each dish, and that they are identical.

If the formula for nitric acid is  $\text{HNO}_3$ , then the following reaction occurred : —



It has already been determined that water is the only other product. But if the formula is  $\text{H}_2\text{N}_2\text{O}_6$  or a higher multiple of this quantity, the reaction should be —



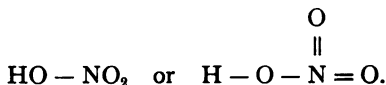
*i.e.* in the dish to which double the quantity of nitric acid was added there should be more salt by mass.

These compounds, if formed, must possess different properties from the one produced in reaction (a) ; but, as we have

seen, these compounds are identical, and it is proper to say that there are no such compounds as have just been indicated, and that the formula for the acids is  $\text{HNO}_3$ . But one series of salts is formed, or the acid is monobasic.

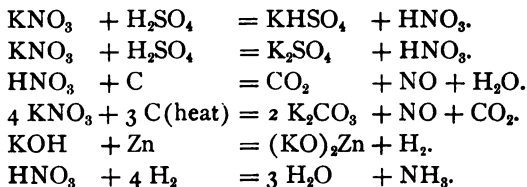
The method just described is often made use of to determine the formula of non-volatile acids.

Nitrogen in this compound is pentivalent; that is, it is regarded as pentivalent, and may be represented thus:—



**Name and History.**—Nitric acid was known to the alchemists as *aqua fortis*, strong water, because of its power to dissolve metals. It was known to the celebrated Geber. The writings of the alchemists give frequent reference to it, and its preparation was described in the fifteenth century by Lully. Its true composition was determined by Cavendish in 1784–85.

#### REACTIONS.



Explain the preceding equations, and balance when necessary.

**Problem.**—How many grammes of potassium nitrate are necessary to produce 1 k. of hydrogen nitrate? How much nitric acid will this make containing 40 per cent of acid?

**Nitrous Acid.**—Nitrous acid can be prepared as explained under nitrogen trioxide. It is very unstable, and can be best



studied in connection with its salts. The solution produced in Experimental Study, No. 46, or a solution of a nitrite like potassium or sodium nitrite, should be examined as follows :—

**Experimental Study, No. 49.** — (a) To 10 cc. of potassium permanganate solution add slowly the nitrous acid solution, or the solution of the nitrite to which acetic acid has been added. Notice the effect on the color of the solution. Prove the presence of nitric acid in the solution. (See TESTS FOR NITRIC ACID.)

(b) Compare this result with the action of nitric acid on the same solution (a). (The nitric acid solution should be very dilute.)

(c) To 10 cc. of a solution of potassium iodide add the nitrous acid solution. Prove that iodine is set free. What are the other products? Test for nitric acid.

(d) Neutralize a portion of the acid solution with potassium hydroxide and evaporate to dryness. Treat a portion of the residue with a drop or so of sulphuric acid. What gas escapes?

(e) Add to a solution of the nitrite a solution of potassium iodide (KI) and follow it by a few drops of acetic acid. Compare with the action of nitrous acid on potassium iodide.

**Properties of Nitrous Acid.**—Nitrous acid has not been separated from its water solution, and its formula  $\text{HNO}_2$  is determined by a study of its salt, its formation from nitrogen trioxide, and the ease with which it is changed to nitric acid.

It is one of the steps in the oxidation of nitrogen to nitric acid. Its salts, the nitrites, are often found in soils and in surface waters. Its presence, therefore, in any appreciable amount in a sample of natural water is evidence that there have been organic nitrogen compounds in the water from which it is produced. The determination of the presence of and amount of the nitrites is therefore considered a matter of importance in the analysis of water that is to be used for drinking purposes.

The presence of any relatively large amount of the nitrites in drinking-water renders it unfit for use, not because of the nitrites themselves, but because their presence indicates the presence of decaying organic matter.

Nitrous acid not only takes oxygen readily from certain compounds forming nitric acid, but it yields oxygen to other compounds under the proper conditions. It is usually itself changed to nitric oxide and water, when it acts as an oxidizing agent.

The nitrites are quite stable in the atmosphere, but are decomposed by acids, even by so weak an acid as acetic acid.

*Tests for Nitrous and Nitric Acid, both when Free and when in Combination.*

1. **Nitrous Acid and Nitrites.** — (a) The free acid decomposes iodides, setting iodine free.

(b) The acid bleaches a solution of potassium permanganate, forming nitric acid.

(c) When the nitrites are acidulated with acetic acid, the solution produces the same result as the free acid.

(d) Dilute inorganic acids decompose the nitrites, setting free the colored oxides of nitrogen.

(e) Nitrites produce a brown colored solution with a solution of ferrous sulphate, intensified by the addition of acetic acid.

2. **Nitric Acid and Nitrates.** — (a) **Brown Ring Test.** — **Experimental Study, No. 50.** — Place in a test-tube 10 cc. of a solution of ferrous sulphate; incline the tube at an angle of  $45^\circ$ , and pour down the side a like volume of sulphuric acid. When the acid has run to the bottom of the tube, bring the tube to a vertical position, and if properly done, the ferrous sulphate solution rests on top of the acid. If the tube is hot, cool it by running cold water on it. When it is cool, bring the tube to an inclined position, and pour down the side the solu-

tion which contains (or which is supposed to contain) the nitric acid or nitrate. Bring the tube to a vertical position, and holding it firmly at the top between the thumb and finger, gently tap the tube at the lower end. If the acid or its salt is present, a brown ring will appear between the two liquids. What is the brown ring? What is the use of the sulphuric acid? What is the use of the ferrous sulphate? Is there any need of the sulphuric acid if the test is made for free hydrogen nitrate?

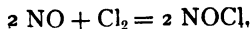
(b) Copper filings are added to the solution of nitrate along with a little sulphuric acid. What are the brown fumes that escape into the air? Explain the use of the sulphuric acid here.

Nitrates are distinguished from nitrites by the action of their solutions on a solution of ferrous sulphate. Nitrates produce no effect on solutions of ferrous sulphate, and nitrites in neutral solutions produce only a slight coloration, if any, in the cold. In the presence of acetic acid nitrites produce a dark brown solution. Nitrates produce no change under the same conditions.

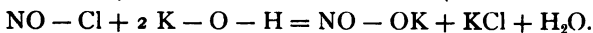
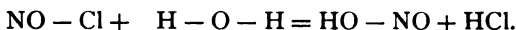
**Experimental Study, No. 51.** — Prove that nitrogen dioxide forms both nitrous and nitric acid when passed into water. Prepare the dioxide as previously described, pass it into water, and exactly neutralize the solution by ammonium hydroxide. Drive off any excess of the alkali, and examine the solution by the method just given. Write all the reactions that occur.

### *Compounds of Chlorine with the Oxide of Nitrogen.*

(a) **Nitric Oxide and Chlorine.** — When nitric oxide (NO) and chlorine are brought together, they unite, forming a compound having the formula NOCl. This compound is a gas having a vapor density of 32.67. It is called nitrosyl chloride, or chloranhydride of nitrous acid. Two volumes of nitric oxide unite with one volume of chlorine: —



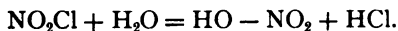
Its action with potassium hydroxide and with water gives a clue to the composition of the nitrites and nitrous acid. With water, it forms nitrous acid and hydrogen chloride. A corresponding action takes place with potassium hydroxide.



Nitrosyl chloride is also formed when nitric and hydrochloric acids are mixed in the production of aqua regia. It is produced by several other methods.

**Problem.**—Nitrosyl chloride has a density of 32.67, and contains 54.13 per cent of chlorine, 21.44 per cent of nitrogen, and 24.43 per cent of oxygen. Atomic masses being known, prove that the formula, according to these facts, should be NOCl.

(*b*) **Nitrogen Dioxide and Chlorine.**—Another compound of chlorine and the oxide of nitrogen is produced by the union of nitrogen dioxide ( $\text{NO}_2$ ) and chlorine gas. The mixed gases are passed through a hot tube, when they unite, 2 vols. of the dioxide entering into combination with 1 vol. of chlorine. The compound has the formula  $\text{NO}_2\text{Cl}$ , and is called nitroxyl chloride or the chloranhydride of nitric acid. It is a very volatile liquid, boiling at  $5^\circ$ . Its vapor density is 40.65. It is decomposed by water into hydrogen chloride and hydrogen nitrate.



Both nitrosyl and nitroxyl chlorides are unstable compounds, giving up their oxygen and chlorine with great readiness.

**Aqua Regia or Nitro-Hydrochloric Acids.**—Aqua regia is a mixture of hydrochloric and nitric acids, and generally it is a mixture of 1 vol. of ordinary nitric acid with 3 vols. of hydrochloric acid. The acids are decomposed and chlorine is set free. Water and nitrosyl chloride are formed, and probably

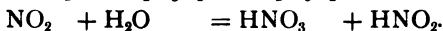
some nitroxyl chloride. The reaction is commonly represented thus :—



If the acids are dilute, only a slight change takes place, even if the mixture is heated. The solvent action of aqua regia is due primarily to the nascent chlorine. This mixture is used to dissolve such metals as gold and platinum, which are not attacked by either of the acids when used alone. The mixture attacks many natural metallic oxides and other substances that resist the action of other substances. The product, when acting on a metal or its oxide, is always the corresponding chloride. Heat is usually necessary to set free chlorine.

The name, *aqua regia*, king of waters, was given to the mixture by Basil Valentine because of its solvent powers.

#### REACTIONS.



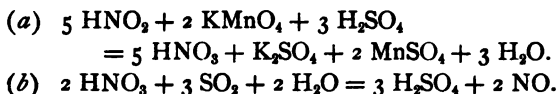
Complete and balance the preceding indicated reactions. Explain the reactions on the basis of chemism.

#### *Oxidation and Reduction.*

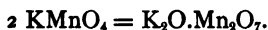
The terms *oxidation* and *reduction* are frequently used in chemistry, and, in their most general sense, refer to the giving to or the taking of oxygen from any substance. Nitric acid readily yields its oxygen to other substances, and is called an oxidizing agent. Sulphur dioxide and sulphurous acid and its salts take oxygen from other compounds, or take up the free element, and is therefore called a reducing agent. The two processes are called oxidation and reduction, respectively.

Oxidation and reduction accompany **each other**; that is, when there is an oxidation of some element, or elements, there is a corresponding reduction of another element, or elements.

## REACTION.



In equation (a) the potassium permanganate ( $\text{KMnO}_4$ ) is rich in oxygen, which it gives up to the nitrous acid, which becomes nitric acid. The compound may be written



In this new combination it is  $\text{MnO}.\text{SO}_3$ . Two atoms of manganese lose five atoms of oxygen, but the five molecules of nitric acid gain five atoms of oxygen. (Students should discuss equation (b). What elements are oxidized? What ones are reduced?)

It can be seen also that there are two elements in each case that change their apparent valence; that is, one element has its valence increased while the other has its valence decreased. It will be noticed that the manganese loses ten units of valence, or, as sometimes called, bonds, according to the method of representation, and that the nitrogen gains ten units of valence, or bonds. (See below for further considerations on the subject.)

*Compounds of Phosphorus and Oxygen and with Oxygen and Hydrogen.*

(a) **The Oxides of Phosphorus.** — It was learned when studying phosphorus that it had great affinity for oxygen as one of its marked chemical properties. It was also learned that it was a

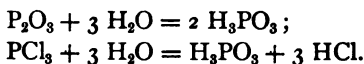
triad in reference to hydrogen. The compound formed with oxygen should, therefore, have the formula  $P_2O_3$  or  $P_4O_6$ . But it has been found that two compounds are formed, depending on the supply of oxygen acting on the phosphorus. To the one formed in a small supply of oxygen the formula  $P_2O_3$  is given, and to the one formed in an unrestricted supply of oxygen the formula  $P_2O_5$  is given, thus giving phosphorus an apparent valence of 3 and 5 in reference to oxygen. This valence, 3 and 5, agrees with the facts found in studying the compounds of phosphorus with the halogens, the compounds  $PCl_3$  and  $PCl_5$  being there pointed out. These two oxides are named phosphorus pentoxide and phosphorus trioxide, in the order mentioned. The phosphorus pentoxide can be distilled unchanged, but no determination of its vapor density has been made.

**Preparation of Phosphorus Trioxide.** — This oxide is prepared by placing pieces of dry phosphorus in a very hard, narrow glass tube, one end of which is drawn to a fine opening, while to the other end is attached an aspirator. The tube is now warmed, and a very slow current of air is aspirated through it. The phosphorus is oxidized and left as a solid in the tube. Bring the compound thus prepared in contact with water, testing the solution with litmus. (Preserve the solution.)

**Properties of the Trioxide.** — This oxide is a white non-crystalline substance. It readily takes up more oxygen, even from the air, and becomes the pentoxide. When brought in contact with water free from dissolved oxygen, a chemical action occurs by which an acid compound is formed. The same acid compound is made when phosphorus trichloride is treated with an excess of water.

From a study of the acid and its salts, and the facts of its formation from phosphorus trioxide and phosphorus trichloride, the formula of the acid is written  $H_3PO_3$ . (See under PHOSPHORIC ACID.)

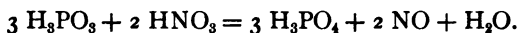
The reactions are : —



**Phosphorous Acid.** — This acid forms salts with many of the bases. It forms two series of salts and is, therefore, dibasic. The third atom of hydrogen does not appear to be replaced by metals. It is true, however, that certain organic bases replace the three atoms of hydrogen.

The salts have the general formula  $\text{M}_2\text{HPO}_3$  and  $\text{MH}_2\text{PO}_3$ , M being any monobasic metal.

**Properties of the Acid.** — Phosphorous acid is a crystalline, glassy-appearing solid. It can be prepared from the water solution by carefully evaporating off the water. It rapidly acquires water from the air. When heated it decomposes into phosphoric acid and phosphide of hydrogen. It also abstracts oxygen from air, and from many compounds containing oxygen, becoming phosphoric acid or its salts. It therefore acts as a reducing agent ; thus : —



## PHOSPHORUS PENTOXIDE.

**Preparation.** — To prepare this oxide, about 1 g. of phosphorus is placed in a dry porcelain evaporating dish or in a porcelain crucible, and the dish is placed on an earthen plate. The phosphorus is ignited and loosely covered with a gas bottle. Again, a piece of phosphorus may be placed in the deflagrating spoon and lowered into a large flask of dry oxygen gas.

**Experimental Study, No. 52.** — (a) Examine and note physical properties.

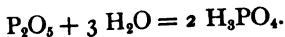
(b) Drop a small amount of the solid into water. Note all the peculiarities, and set the solution aside for further examination.



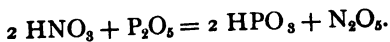
(c) Dissolve a portion of the oxide in hot water, and another portion in ice-cold water. Set aside for further examination. Examine each solution with blue litmus paper.

(d) Heat a little of the oxide in a test-tube, noticing its vaporization.

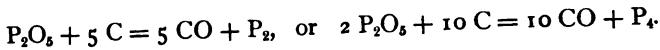
**Properties of Phosphorus Pentoxide.** — Phosphorus pentoxide is a white amorphous solid. It unites with water with great avidity, the solution becoming acid. It rapidly absorbs water from the atmosphere, and is often used to dry gases and liquids. The reaction is : —



It is used to remove water from acids, such as nitric acid ; thus : —



When heated with carbon it gives up its oxygen, forming carbon monoxide (CO), the phosphorus being set free.



In this reaction 10 vols. of carbon monoxide are formed to 1 vol. of phosphorus vapor, or, applying Avogadro's law, 10 molecules of carbon monoxide are formed for every molecule of phosphorus. Ten molecules of carbon monoxide contain the equivalent of five molecules of oxygen. It may be said, therefore, that five molecules of oxygen unite with one molecule of phosphorus to form this oxide. Accordingly the formula should be either  $\text{P}_4\text{O}_{10}$  or  $\text{P}_2\text{O}_5$ . Considered in reference to its valence, as has been shown in the case of phosphorus pentachloride, the latter formula is taken as the correct representation of the molecule.

**Acids Formed from Phosphorus Pentoxide.** — **Experimental Study, No. 53.** — (1) A study of the solution of the oxide prepared by treating it with cold water,  $0^\circ$  to  $10^\circ$ .

(a) Make a solution in water of the white of an egg, and add a few drops of it to the acid solution. Note the effect on the albumen of the egg.

(b) Treat 10 cc. of the acid solution with a solution of silver nitrate and note the color of the precipitate formed.

(c) To 10 cc. of the acid solution add a solution of ammonio-silver nitrate. (This latter solution is prepared by adding ammonia hydroxide to a solution of silver nitrate until the precipitate, which is formed at first, is just dissolved.)

(d) To 10 cc. of the acid solution add 10 cc. of a solution of molybdate of ammonia. Note the precipitate formed, the peculiarities of its formation, color, etc.

(e) Boil a portion of the acid solution for from three to five minutes. Make up the volume lost by evaporation and test it in the manner just described in (a), (b), (c), (d), noting the differences in the results.

(2) Prepare a solution of the pentoxide by dissolving it in hot water, and examine in the same manner as (1). Note and describe the results in each case.

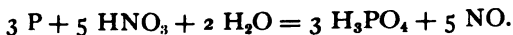
**Experimental Study, No. 54.** — Boil 1 g. of red phosphorus in 25 cc. of nitric acid, regulating the heat by the rapidity of the action. This is best done in a 100 cc. flask fitted with a rubber stopper holding a vertical glass tube 40 to 50 cm. long. What gas escapes?

When the phosphorus is dissolved boil the solution in an open dish to remove excess of nitric acid. Neutralize and test portions of the solution according to (2).

Evaporate off the water and heat the residue to redness and examine and describe it. Dissolve a portion of the solid residue in cold water. Neutralize and test the solution according to (1). Dissolve another portion in hot water and treat according to (2). Note results in each case.

**Phosphoric or Ortho-Phosphoric Acid.** — **Methods of Preparation.** — This acid is formed when the pentoxide of phos-

phorus is dissolved in hot water. It is also formed when phosphorus is boiled with nitric acid. The reaction is—



Phosphoric acid is the product of the oxidation of all the lower acids of phosphorus. The acid is obtained from its water solution by evaporating at temperatures not much above  $100^\circ$ , and never at temperatures above  $210^\circ$ . The acid crystallizes in colorless crystals that are quite hard. In the air the crystals absorb water and form a thick, syrupy, acid liquid. When this acid is analyzed quantitatively, it is found to contain 65.3 per cent of oxygen, 31.63 per cent of phosphorus, and 3.7 per cent of hydrogen. It has been further found that sodium and potassium each form three salts with this acid, or the hydrogen can be replaced by three monad bases. The hydrogen can be said to exist, therefore, in at least three atoms in the molecule of the acid, since one atom of sodium or potassium replaces one atom of hydrogen.

If a solution of the pure acid is treated with sodium or potassium carbonate until it is neutral, and the excess of water allowed to escape, there crystallizes out a compound which yields upon analysis sodium (or potassium), hydrogen, phosphorus, and oxygen. The amount of hydrogen is only one-third of the original amount found in the acid. If this compound called disodium hydrogen phosphate, is dissolved in water and sodium (or potassium) hydroxide is added, there is formed a compound that contains no hydrogen but does contain one-third more of the alkali base.

Again, if the sodium hydrogen phosphate is dissolved in water and treated with phosphoric acid, there is formed a compound which contains one-half as much of the alkali base and twice as much hydrogen as the original compound. Each of the compounds differs from all the others in crystalline form and in other properties.

There are at least, therefore, three atoms of hydrogen to the molecule of acid. In every 100 parts by mass, as has been just stated, there are 3.07 parts of hydrogen, 31.63 parts of phosphorus, and 65.3 parts of oxygen. Now if each of these numbers be divided by 1.023 (that is, a number that changes 3.07 to 3), these numbers become 3, 30.91+, 63.83+, respectively. Taking 3 as representing three atoms of hydrogen, the other numbers correspond to one atom of phosphorus and four atoms of oxygen, and the formula for the acid is  $H_3PO_4$ .

This acid is called orthophosphoric acid, or simply phosphoric acid. The prefix *ortho* signifies straight or right, and refers to the fact that this is the normal phosphoric acid, in the sense that it is always the product of the complete oxidation of phosphorus in the presence of water.

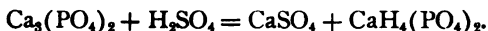
The salts of sodium, above referred to, are consequently represented by the formulæ  $NaH_2PO_4$ ,  $Na_2HPO_4$ , and  $Na_3PO_4$ .

They are named sodium dihydrogen phosphate, disodium hydrogen phosphate, and sodium phosphate, in the order named.

**Tests.** — A solution of the acid or, better, a solution of the salt of the acid, produces a yellow precipitate with silver nitrate. A solution of molybdate of ammonium produces a yellow precipitate with soluble phosphates and phosphoric acid. This latter test distinguishes this acid and its salts in solution from all others (except arsenic acid and its salts). This acid does not coagulate albumen.

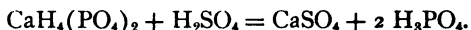
**Natural Sources of Phosphoric Acid.** — Under the topic PHOSPHORUS the relation of this element to plant and animal life was in part pointed out. It was there shown what the cycle of chemical changes is that this element is constantly undergoing. It is there pointed out that animals, especially vertebrated animals, store up a large amount of the phosphorus in the form of calcium phosphate. When these bones are heated in the air, the organic matter is decomposed and oxy-

dized, and the residue, called bone-ash, is nearly pure normal calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ). This bone-ash is treated with sulphuric acid, when the following reaction takes place :—



Calcium sulphate ( $\text{CaSO}_4$ ) is insoluble, while the calcium tetrahydrogen phosphate is soluble. The latter compound is sometimes called the soluble phosphate, or "superphosphate," and in this condition is used as a fertilizer. Plants require that substances shall be in solution before their rootlets will absorb them. Usually the calcium sulphate is not removed in preparing the bone-ash of fertilizers, but the mixture is broken up and used unchanged. Ordinarily, insoluble phosphates are slowly rendered soluble under the conditions that obtain in soils, so that ground-up bones are sometimes used as a fertilizer without further treatment.

When the soluble superphosphate ( $\text{CaH}_4(\text{PO}_4)_2$ ) is dissolved in water, most of the calcium sulphate ( $\text{CaSO}_4$ ) is left undissolved, and can be separated by filtration. The solution is evaporated to dryness, and the residue is treated with more sulphuric acid, when the decomposition is completed thus :—



The remainder of the sulphate is removed by filtration, and water and alcohol added to dissolve the phosphoric acid. From the alcohol solution it is separated out by evaporating off the alcohol.

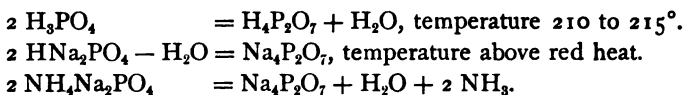
The acid prepared in this way is not quite pure, since the bone-ash is not pure normal calcium phosphate, but contains a small amount of magnesium phosphate and calcium carbonate and other impurities.

There are also large natural deposits of impure phosphate in North and South Carolina and in Florida. The natural phosphates are known as phosphorite, apatite, coprolite.

They are supposed to have their origin from the bones of animals.

Guano owes its value in part to the calcium phosphate which it contains.

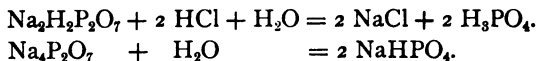
**Pyrophosphoric Acid.** — Pyrophosphoric acid was discovered by Clark in 1826. When he heated phosphoric acid to 210 to 215°, for some time a modification of the acid was produced, which proved to be tetrabasic. It is also produced by igniting the dimetallic phosphate or the trimetallic salts, in which ammonia displaces one of the atoms of hydrogen. The step to the removal of water from the acid, and the changes produced in certain of the salts by means of heat, may be represented thus : —



The acid generally exists in solution, but may be obtained by evaporation at a temperature not above 215°. It is a soft, glassy, semi-crystalline substance. Its four atoms of hydrogen can be replaced by bases, either wholly or in part. The acid thus forms four possible series of salts.

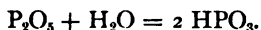
The name *pyrophosphoric* acid was given to the compound by Clark. The prefix *pyro* signifies fire, and was applied to the acid because it was produced from phosphoric acid by heat.

The salts of the acid are changed into phosphates by boiling them in acids, or by evaporating their solutions to dryness.

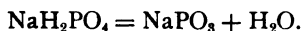
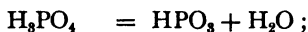


**Metaphosphoric or Glacial Phosphoric Acid.** — This acid is formed in several ways. It is prepared from phosphorus pent-

oxide, when it is dissolved in cold water, temperatures being between  $0^{\circ}$  and  $30^{\circ}$ . The reaction is written thus :—



It can also be prepared by evaporating off the water from a solution of phosphoric acid and heating the residue to a temperature of  $400^{\circ}$ . Salts of the acid are prepared from dihydrogen phosphates by heating them to high temperatures, usually above red heat, when a molecule of water escapes. These reactions may be represented as follows :—



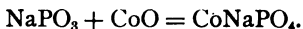
This acid is a solid, transparent and glass-like in appearance. It rapidly absorbs water (or deliquesces) in the air. The solution of the acid takes up more water when boiled, and becomes phosphoric acid. The salts are fairly stable, but can be converted into the orthophosphates by boiling their water solution.

The acid and its salts are distinguished from the other acids of phosphorus by its action on albumen and on the ammonium silver nitrate solution. It coagulates albumen, and produces a white precipitate (soluble in the excess of the reagent) with the ammonio-silver nitrate solution.

When the salts of metaphosphoric acid are heated with the oxides of metals, the salts fuse and unite with the oxide, forming the phosphate. In case of many oxides, characteristically colored masses, called beads, are produced. For example, when oxide of cobalt is thus heated, a blue glassy mass is formed. The metaphosphate for this bead test is usually prepared by heating sodium ammonium hydrogen phosphate, or microcosmic salt. The changes produced by the first heating are represented thus :—

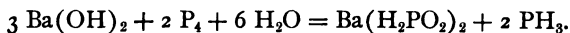


And the final change is represented thus : —

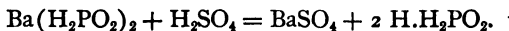


The acid was first prepared in 1833, by Graham, by heating phosphoric acid to the temperature just indicated.

**Hypophosphorous Acid and its Salts.** — In the preparation of phosphide of hydrogen a compound is formed which, when separated out by evaporating off the water, is found to contain potassium, hydrogen, phosphorus, and oxygen. This compound possesses different properties from any of the other compounds containing the same elements. For example, the acid and its compound are not very stable, and are easily converted into the phosphate, or phosphoric acid, by oxydizing agents. It contains relatively a smaller amount of oxygen than any other compound of the same elements. Its formula has been determined to be  $\text{KH}_2\text{PO}_2$ . If barium hydroxide ( $\text{Ba}(\text{OH})_2$ ) is used in place of potassium hydroxide in the preparation of phosphide of hydrogen, a similar barium salt is produced.

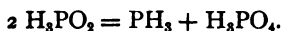


The barium hypophosphite is soluble in water. The excess of the barium hydroxide is removed by passing through the solution carbon dioxide, which forms an insoluble compound with the barium of the hydroxide, barium carbonate ( $\text{BaCO}_3$ ), but does not decompose the hypophosphite. This insoluble substance is filtered out and the solution concentrated, when the hypophosphite of barium crystallizes out. The acid is obtained from this salt by treating its solution with just sufficient of dilute sulphuric acid to unite with all the barium of the salt, forming an insoluble compound, — barium sulphate ( $\text{BaSO}_4$ ). The hydrogen of the sulphuric acid takes the place of the barium in the hypophosphite.





The sulphate is filtered out, and the solution of the acid concentrated under reduced pressure. The acid is a thick liquid, having strongly acid properties. When this liquid acid is cooled down to zero, it forms leaf-like crystals, which melt at a temperature of  $17.4^{\circ}$ . At higher temperatures it decomposes into phosphide of hydrogen and phosphoric acid.

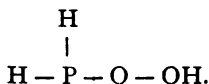


Notice that no new elements are added to the molecule, but that the change is the rearrangement of the atoms of the molecule under the influence of heat. The most characteristic property of the acid is its tendency to take up oxygen and become phosphoric acid; that is, for the phosphorus to pass from its lowest valence, of 1, to its highest valence, of 5. It is, therefore, a powerful reducing agent. (How would it act with nitric acid? What are the products?)

It reduces sulphuric and sulphurous acids, or the sulphur of these acids, to free sulphur. It also reduces many metals from their salts; *e.g.* mercury, gold, and silver.

The salts of the acid are decomposed at red heat, producing phosphide of hydrogen and the metallic phosphate or pyrophosphate.

But one atom of the hydrogen can be replaced by metals. It is supposed to contain but one hydroxyl group, and is commonly represented —



The acid and its salts may be recognized by the products of their decomposition by heat, and their reducing action on the compounds previously mentioned.

Phosphorus forms compounds with sulphur and nitrogen, but they are not of sufficient importance to be studied here.

**Valence of Phosphorus.** — The formula determined for hydro-

gen phosphide indicates that the valence of phosphorus with hydrogen is 3. It has also been noted that the element forms two compounds with most of the halogens, which, measured in the same manner as was the hydrogen compound, shows that the element has a valence of 3 and 5 towards this group of elements. With oxygen, phosphorus forms two compounds having the formulæ  $P_2O_3$  and  $P_2O_5$ , the valence of phosphorus being 3 and 5 respectively, considering the valence of oxygen as fixed at 2. The oxide corresponding to hypophosphorous acid should have the formula  $P_2O$ . This latter oxide has not been prepared. Granting that phosphorus has a valence corresponding to this oxide, then its valence varies from 1 to 2, to 5. The valence of phosphorus in hypophosphorous acid is therefore 1; in phosphorous acid, 3; in the phosphoric acid, 5.

A very helpful convention in reference to the valence of elements in compounds is to consider that certain elements have a fixed valence; that certain elements are always positive while others are always negative; and further, that the algebraic sum of these units in any compound is always equal to zero. Thus by the use of a few simple rules the valence of the elements of any inorganic compound can be easily determined. These rules, which are due to Professor O. C. Johnson, are:—

(a) The algebraic sum of the valences of the elements of any inorganic compound is always zero.

(b) The valence of oxygen is always negative, and 2.

(c) The valence of hydrogen is always positive, and 1.

(d) The metals are nearly always positive, and are always positive when they act as bases.

(e) Uncombined elements have no units of valence employed, and the valence may be said to be zero.

(f) Acid radicals are always combined with hydrogen or with a metal, and are consequently negative.

If we examine the formula for hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ), it is readily seen that phosphorus has a positive valence of 1. For example, there are four negative valences due to oxygen, and three positive valences due to hydrogen, and therefore phosphorus has one positive valence, since  $3 + 1 - 4 = 0$ . In the other acids of phosphorus, by the same method of estimation, the valences of the element are 3 and 5 (positive), respectively.

When the valence of phosphorus changes, it increases by twos. In general, starting with either of the lower acids of phosphorus, the valence always changes to the highest number, 5, when they are acted upon by some oxidizing agent.

If the following rule be added to those just given, the balancing of equations in which oxidation and reduction occur becomes a very simple matter. The terms *oxidation* and *reduction* require a slightly changed meaning from the common use of the terms, in order to understand the application of the rule. Oxidation signifies, with this new meaning, the increasing of the number of units of valence that any atom has, whether free or combined. Reduction signifies the opposite change.

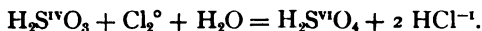
The rule is stated thus : —

When any chemical reaction occurs in which oxidation and reduction take place, then the number of units of valence apparently lost by one or more kinds of atoms or groups of atoms are gained by one or more other atoms or kinds of atoms or groups of atoms.

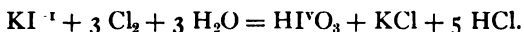
If, therefore, in any chemical reaction of the character just pointed out, the products of the change are known, the equation can be easily balanced by determining the loss or gain in any valence as indicated in the rule and thus taking a sufficient number of atoms of the element or elements that lose (or gain) valence to equal the number of units gained (or lost) by the other atom or atoms.

The application of these rules is shown in the following examples : —

When chlorine acts on sulphurous acid (or its salts), it is changed to sulphuric acid and the chlorine becomes hydrogen chloride.



The sulphur of the sulphurous acid has a valence of +4; but in its changed condition it has a valence of +6. Each atom of sulphur has, therefore, gained two units of valence. Chlorine loses for each atom one unit of valence, since in hydrogen chloride it has a valence of -1, and no units of valence in its free condition. The two atoms in the molecule of chlorine lose, therefore, two units of valence. Therefore one molecule of each substance is used.



Here iodine gains six units of valence, and each molecule of chlorine loses two units. Therefore three molecules of chlorine are required for each molecule of iodide.

*Compounds of Arsenic with Oxygen, and with Oxygen and Hydrogen.*

(1) **Arsenious Oxide. — Occurrence.** — Arsenious oxide occurs in small quantities in nature in the mineral known as arsenolite. Most of the commercial article is a by-product, produced when the ores of certain metals are roasted, such as iron and copper ores, which often contain arsenic.

**Methods of Preparation.** — Oxygen readily unites with arsenic at high temperatures, the product being a gas at the temperature of formation. The oxide is commonly prepared by heating in a reverberatory furnace the mineral having the formula FeAsS. The oxygen of the air unites with the elements of the ore, forming oxides. The oxides of arsenic and sulphur, being gases, escape, but the oxide of arsenic condenses

in the cool part of the apparatus, while the sulphur dioxide escapes through the flues.

**Preparation.** — (Review ARSENIC, on page 159.) Powder some of the element arsenic, and heat it in an open tube in the air or (better) in oxygen. Notice the white powder deposited on the sides of the tube. Of what must the compound consist?

Next heat in a tube open at both ends an ore containing arsenic, like the one just mentioned ( $\text{AsFeS}$ ). The tube should be placed at an angle of  $45$  to  $60^\circ$  to the horizontal plane. The powdered ore is placed near the lower end of the tube, which should be 25 cm. long, 10 mm. wide. This process is technically called roasting. Notice the escaping gas. What is it?

**Experimental Study, No. 55.** — (a) Examine the white deposit on the sides of the tube with a hand magnifier. Note the crystalline form.

(b) Remove the white powder just prepared (or use the oxide furnished you), and boil (say) 1 g. in 200 cc. of water, for some time, or until it disappears. Add more water if necessary. Note the action of the oxide towards water. Does it sink in the water immediately? Examine the solution with litmus paper.

(c) Evaporate a portion of the clear solution carefully; that is, do not heat the residue much above boiling-point. What does the residue appear to be? Has it formed a permanent compound with the water? Compare it with phosphorus and sulphur oxides in reference to this point.

(d) Add hydrochloric acid to a portion of the water solution, and pass hydrogen sulphide into it for a short time, or until the solution becomes saturated with the gas. Note the precipitate, its color, etc. It is sulphide of arsenic.

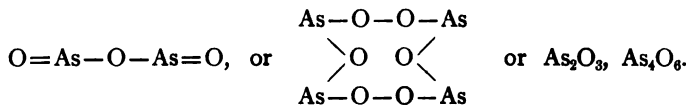
(e) Review the experimental study when arsenide of hydrogen was produced. (See page 163.) How does the nascent hydrogen act on the oxide of arsenic?

(f) Heat the mixture of the oxide of arsenic and carbon in a dry tube. What is the deposit on the tube? What has become of the oxygen?

(g) Add the oxide to the boiling solution of potassium hydroxide as long as any dissolves. Evaporate to dryness, and compare the product with the oxide and with potassium hydroxide. What is the action of potassium hydroxide on acid-forming oxides?

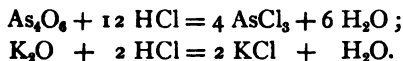
**Physical Properties.** — Arsenious oxide is a solid, amorphous or crystalline, according to the method of preparation. If it is formed by sublimation, it occurs in octahedral crystals on the walls of the cooling chamber. However, if the temperature of the condensing walls is but little below the temperature of condensation, it is deposited in an amorphous, glassy mass. The amorphous variety slowly changes its structure, becoming crystalline; losing its glassy appearance, it becomes opaque.

The vapor density of the oxide at  $1560^{\circ}$  is 198. The compound contains 75.75 per cent of arsenic and 24.25 per cent of oxygen, and therefore corresponds to the formula  $\text{As}_4\text{O}_6$ . Show how. This formula or its half ( $\text{As}_2\text{O}_3$ ) is used to represent a molecule. Either formula agrees with that indicated by the hydrogen valence of arsenic, as seen in the compound  $\text{AsH}_3$ . The compound may be represented thus:—



The oxide is converted into a colorless vapor at  $218^{\circ}$ . It is slightly soluble in water, especially after long boiling. The water solution is faintly acid to litmus, indicating that a new compound has been formed with the water, since the dry oxide does not produce any acid reaction. The glassy variety is more soluble than the crystalline form.

**Chemical Properties.** — Arsenious trioxide is quite soluble in concentrated hydrochloric acid, acting like the oxides of most of the bases. The reaction may be represented thus : —



However, the chloride is not usually prepared in this way. It is also true that the chloride is decomposed by much water, reversing the above reaction.

The oxygen of arsenic trioxide is easily removed, or it is reduced by many other elements that have a great affinity for oxygen. In Marsh's test the hydrogen takes the oxygen, and gives hydrogen to the arsenic. Carbon and hydrogen sulphide act in a similar way.

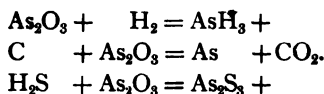
**Poisonous Properties.** — The oxide of arsenic is what is known in commerce as arsenic. It is very poisonous when taken into the system, especially when taken into the stomach, a fatal dose being from 225 to 450 mg. (two to four grains). Owing to the slow solubility of the oxide, its effects are not felt immediately. Nausea, vomiting, and violent pains in the abdominal region are some of the effects of the poison. Death is frequently preceded by convulsions. The antidote for arsenic poisoning is to produce vomiting if possible, and give freshly precipitated ferric hydroxide. (See under the study of iron for the method of preparation of the latter compound.) Ferric hydroxide forms an insoluble compound with the oxide of arsenic.

**Name and History.** — Arsenic trioxide has been known from the early times. Its presence in various ores and its ready oxidation made it present as a by-product when such ores were roasted.

It has been variously named arsenic, white arsenic, arsenic acid, and arsenious oxide. According to the system of nomenclature adopted, it should be named arsenious oxide or trioxide of arsenic (hexoxide).

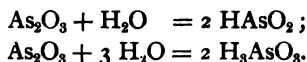
**Uses.** — Arsenic trioxide has many uses in the arts and manufactures. It is used in preparing several pigments and other compounds containing arsenic, such as Paris green and Scheele's green. It is used to destroy the green color of glass, especially when the green color is due to iron compounds. At the temperature of the fusion of the glass, the arsenic compound yields oxygen to the iron compound, forming a compound which is colorless.

## REACTIONS.



Complete, and explain preceding incomplete equations.

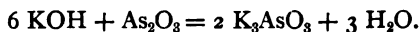
**Arsenious Acid.** — When the oxide of arsenic reacts with water, the following changes are supposed to occur : —



The acid has not been separated from the water holding it in solution, since it is decomposed when the water is removed. But with bases it forms salts, indicating that there are one or three atoms of hydrogen in the molecule. With potassium, for example, it forms a compound  $\text{KAsO}_2$ , when there is an excess of the acid or the oxide used. Thus : —



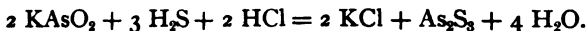
With an excess of the alkali present, the reaction is —



The acids corresponding to the two salts are called meta-arsenious acid ( $\text{HAsO}_2$ ) and arsenious acid ( $\text{H}_3\text{AsO}_3$ ). In case of the latter acid, normal and acid salts are formed.



(Name the salts formed with sodium and potassium.) This acid or its salts, in acidified solution, are decomposed by hydrogen sulphide with the formation of sulphide of arsenic or arsenious sulphide.



Explain the use of the hydrogen chloride. Which compound is usually more stable, an acid or its potassium salt?

With silver nitrate arsenites precipitate a yellow compound, silver arsenite ( $\text{AgAsO}_2$ , or  $\text{Ag}_3\text{AsO}_3$ ).

The arsenites are all very poisonous; especially is this true of the readily soluble salts. The arsenites in solution are decomposed by nascent hydrogen, forming the hydride of arsenic ( $\text{AsH}_3$ ). Arsenious acid and its salts readily take oxygen from oxidizing agents, forming compounds in which the apparent valence of arsenic is 5.

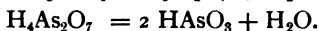
**Arsenic Oxide. — Its Corresponding Acids and Salts.** — When arsenic is oxidized in the air, but one compound is produced under any conditions; that is, arsenic trioxide ( $\text{As}_2\text{O}_3$ , or  $\text{As}_4\text{O}_6$ ). In this respect, arsenic differs from phosphorus and resembles sulphur. If, however, the oxygen is acted upon by some oxidizing agent in the presence of water, it takes up two atoms more of oxygen. The action of nitric acid on the oxide may be taken as an example of the effect of an oxidizing agent in general: —



If now the solution is evaporated to dryness and then heated to  $275^\circ$ , there remains a compound represented by the formula  $\text{As}_2\text{O}_5$ . If this oxide is heated to bright redness, it decomposes into oxygen ( $\text{O}_2$ ) and the trioxide ( $\text{As}_2\text{O}_3$ ). Reducing agents produce the same result, appropriating the oxygen thus given up.

**Properties.** — The pentoxide of arsenic is a solid which

dissolves in water, forming an acid solution, which on evaporation yields a solid body having a formula  $\text{H}_3\text{AsO}_4$  or  $(\text{HO})_3\text{AsO}$ . This acid acts like phosphoric acid when heated; that is, it loses water, and an acid containing relatively less hydrogen and oxygen is formed. At  $180^\circ$ , one molecule of water escapes from two molecules of acid, and pyroarsenic acid ( $\text{H}_4\text{As}_2\text{O}_7$ ) is formed. At  $200^\circ$  the pyroarsenic changes to meta-arsenic acid ( $\text{HAsO}_3$ ).



These acids, however, when treated with water change to the tribasic acid ( $\text{H}_3\text{AsO}_4$ ). The salts of these acids also when put in solution in water return to the normal tribasic form. The salts of the tribasic acid are both normal and acid. They are with sodium,  $\text{Na}_3\text{AsO}_4$ ,  $\text{Na}_2\text{HAsO}_4$ , and  $\text{NaH}_2\text{AsO}_4$ .

Hydrogen sulphide slowly reduces the arsenates in acid solution, and there is formed arsenious sulphide ( $\text{As}_2\text{S}_3$ ) and free sulphur, and not arsenic sulphide ( $\text{As}_2\text{S}_5$ ).

The solutions of the salts of arsenic acid produce a brick-red precipitate with a silver nitrate solution, silver arsenate ( $\text{Ag}_3\text{AsO}_4$ ). Molybdate of ammonia solution produces a yellow precipitate much resembling the precipitate produced by the same agent with phosphates. They can be distinguished when both the phosphate and arsenate are present, by reducing and separating out the arsenic by means of hydrogen sulphide, and then testing the solution remaining for phosphates, as has been previously described. The arsenic compound can be reduced easily by sulphur dioxide to the arsenious form.

**Valence of Arsenic.**—The apparent valence of arsenic is 3 and 5, as is shown by its hydrogen compound and by its compounds with oxygen. It should be noted that oxidizing and reducing agents, acting in the wet way, change its valence between these two numbers.

*Compound with Sulphur and Arsenic.*

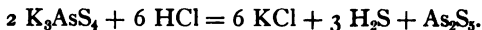
Sulphur forms three compounds with arsenic, which are represented by the formulæ  $\text{As}_2\text{S}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{As}_2\text{S}_5$ . These sulphides are named disulphide, trisulphide, and pentasulphide of arsenic, respectively. The latter two sulphides are similar in form to the oxides of arsenic. In fact, sulphur seems to take the place of oxygen in several compounds; that is, salts of arsenious and arsenic acid have corresponding to them compounds in which sulphur takes the place of the oxygen. For example,  $\text{KAsO}_2$  and  $\text{KAsS}_2$ ;  $\text{K}_3\text{AsO}_3$  and  $\text{K}_3\text{AsS}_3$ ;  $\text{K}_3\text{AsO}_4$  and  $\text{K}_3\text{AsS}_4$ , are illustrations of such corresponding compounds. These salts are called sulpharsenites and sulpharsenates.

The disulphide of arsenic is found in nature, and is known as realgar. It is produced by heating sulphur and arsenic together in proportions of 75 parts of arsenic to 32 parts of sulphur. The compound, which is an orange-red solid, is used as a pigment, and to produce what is called white or Indian fire. When used to produce Indian fire, it is intimately mixed with potassium nitrate ( $\text{KNO}_3$ ). (What are the products of the decomposition of this mixture? What is the use of the potassium nitrate in the mixture?)

**Arsenic Trisulphide.** — As has been already seen, this compound is formed when hydrogen sulphide acts on a solution of an arsenite or on a solution of arsenious acid. It is a lemon-yellow solid, and is commonly called orpiment (*auri-pigmentum*) or gold pigment. It is also prepared by heating sulphur and arsenic in the proper proportions. (What are the proper proportions?) It is used, in a finely divided condition, as a pigment.

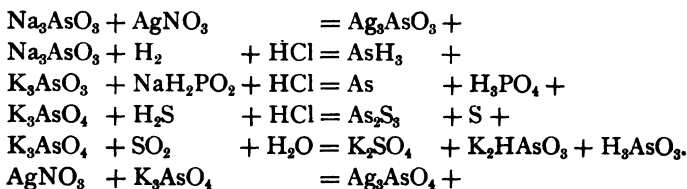
**Arsenic Pentasulphide.** — The pentasulphide of arsenic is not formed by the action of hydrogen sulphide on arsenic acid, or its salts, but is produced by heating together sulphur and arsenic

in the proper proportions. (Determine what these proportions must be.) It is also produced when the compound sulpharsenate of potassium ( $K_3AsS_5$ ) is treated with hydrochloric acid, thus : —



The sulphides of arsenic are all insoluble in water.

#### REACTIONS.



#### *Compounds of the Halogen Elements with Oxygen, and with Oxygen and Hydrogen.*

**General Statement.** — Oxygen forms no known compounds with fluorine, but does form compounds with all the other halogens. None of the compounds of the halogens are found ready formed in nature, owing to the weak affinity between these elements and oxygen. They are unstable, and are not easily prepared.

**Chlorine Monoxide or Hypochlorous Oxide.** — **Preparation.** — Chlorine does not unite directly with oxygen under ordinary conditions. If the dry chlorine gas be passed over cold red oxide of mercury, a portion of the chlorine unites with the mercury, and another portion unites with the oxygen. An interesting fact is that the crystalline oxide of mercury is not decomposed by the chlorine, while the dry precipitated oxide is decomposed. (Explain why it is so. What is the difference between the two conditions of the oxide as to struc-

ture?) Great care is required in the manufacture of pure oxide.

Owing to the difficulty of preparing and experimenting with the chlorine monoxide, its experimental study is omitted.

**Physical Properties.** — Chlorine monoxide is a very unstable gas soluble in water, and resembles chlorine in many of its properties. At a very low temperature it is condensed to a reddish liquid, which boils at  $-20^{\circ}$ . The gas is so unstable that a slight rise in temperature, even that produced by the warmth of the hand, causes it to decompose into chlorine ( $\text{Cl}_2$ ) and oxygen ( $\text{O}_2$ ). Exposure to sunlight produces violent explosions. One litre of the gas on decomposition becomes 1 l. of chlorine and  $\frac{1}{2}$  l. of oxygen. Its vapor density is 43.37. It is very soluble in water; 1 cc. of water dissolves 20 cc. of the gas, producing a yellow-colored solution.

**Chemical Properties.** — Owing to the ease with which this compound is decomposed, it acts as a strong oxidizing agent, resembling chlorine, only it is much more powerful in its action. This is due to several facts. For example, when the oxide decomposes, the nascent chlorine produces its effects more powerfully because it is in this condition, and the oxygen, which in general is the real oxidizer when chlorine is used to oxidize, is also in the same nascent condition. The heat of formation of monoxide of chlorine is  $-17,930$  calories; when, therefore, the compound is decomposed, a large amount of heat is evolved.

With water it forms an acid compound, illustrating the general action of water on the acid family of oxides.

**Determination of Molecular Formula.** — **Facts.** — (a) Analysis shows that the oxide contains 81.52 per cent of chlorine, and 18.48 per cent of oxygen.

(b) The vapor density of the compound is 43.37.

(c) The atomic masses of the elements are known.

(d) One litre of the gas contains 1 l. of chlorine and  $\frac{1}{2}$  l. of

oxygen. From these facts show that the percentage is as is stated in (a).

**Problem.** — From the facts stated show that the formula for the oxide is  $\text{Cl}_2\text{O}$ . Also show how the fact (c) corroborates this determination.

**Hypochlorous Acid.** — **Preparation.** — Hypochlorous acid can be prepared in a water solution in a sufficient quantity to study some of its properties in the following manner : —

A litre flask is filled with chlorine gas, and to it is added 1 gr. of precipitated oxide of mercury (mercuric oxide) and 20 cc. of water. Cork the flask tightly and shake thoroughly until the oxide becomes black. Decant off the greenish yellow liquid and examine its properties.

**Experimental Study, No. 56.** — (a) Examine and note physical properties.

(b) Boil 5 cc. of the liquid in a test-tube and note the gas or gases that escape. What is left in the tube? Test it with a silver-nitrate solution. What does this prove as to the way the chlorine is combined in the boiled solution?

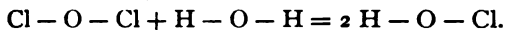
(c) Test its bleaching action on unbleached cotton goods.

(d) Treat solutions of indigo, logwood, and cochineal with some of the solution of the hypochlorous acid.

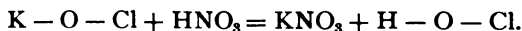
(e) Pass chlorine gas into 30 to 50 cc. of a cold solution of potassium hydroxide as long as the gas is absorbed, or until the solution is slightly tinged with the color due to chlorine gas. By passing air through the solution for a few minutes the free chlorine can be removed. The solution should be colorless. When colorless, test 10 cc. of the solution with a few drops of any acid. What is the change? Warm the solution. What gas escapes? In 10 cc. of the solution dip some colored cotton goods. Add a few drops of acid, and again dip in the colored goods. Test some of the solution that is free from uncombined chlorine with silver-nitrate solution. Note the result. Next, treat a portion of the solution with the silver solution as

long as any precipitate is formed. Filter out this precipitate and to the filtrate add a few drops of sulphuric acid. Explain the results.

**Physical and Chemical Properties.** — Hypochlorous acid is known only in its water solutions, but its salts are well known. Its aqueous solution is prepared by passing chlorine monoxide into water, when the following reaction occurs : —

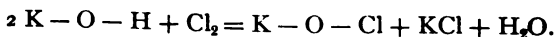


A dilute solution (not over 5 per cent of the free acid) may be produced by treating a solution of one of its salts like potassium hypochlorite with a dilute solution of nitric acid, and distilling.

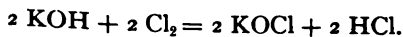


When chlorine gas acts upon water, oxygen is set free and hydrogen chloride is formed. (Compare this action with the action of potassium or sodium on water.)

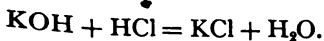
When chlorine gas is passed into a solution of potassium hydroxide in the cold, one atom of the molecule of chlorine takes the place of the hydrogen of the hydroxyl, while the other unites with one atom of potassium; and water is formed as a by-product.



It is probable that the first change may be represented thus : —



The hydrogen chloride thus formed immediately reacts with more of the potassium hydroxide, forming potassium chloride and water.

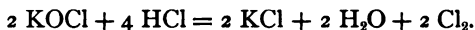


The knowledge of the composition of this acid is gained from the study of its salts, the hypochlorites. But one salt is

formed with potassium and sodium, or the acid is monobasic. No hydrogen has ever been found in any of the salts of this acid.

An analysis of the potassium salt shows that it contains 43.175 per cent of potassium, 39.856 per cent of chlorine, and 17.669 per cent of oxygen. Now, since this acid is monobasic, the amount of potassium corresponds to one atom of hydrogen. Dividing the per cents just given by 1.107, the numbers representing the per cents become 39, 35.37, and 15.96. These numbers correspond to one atom of each element, and the formula for the salt is  $\text{KClO}$ , or for the acid it is  $\text{HClO}$ .

These salts are easily decomposed by any acid, chlorine being set free, and a salt corresponding to the decomposing acid is formed.



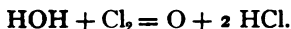
This property of hypochlorites determines their use as a storehouse for chlorine gas; that is, determines their use as bleaching agents, disinfectants, etc. The active part of bleaching-powder is calcium hypochlorite ( $\text{Ca}(\text{ClO})_2$ ). (See under **CALCIUM** for preparation of bleaching-powder.)

It should be noticed that an acid like hydrochloric acid must be used if the chlorine is desired quickly or in any quantity from bleaching-powder. It slowly decomposes in the air, but not with sufficient rapidity to be useful for purposes of disinfection, bleaching, etc.

Under the study of chlorine, it was noted that in many cases of bleaching by it, it was oxygen that did the bleaching; that the moisture, necessarily present, was decomposed by the chlorine, and that free oxygen and hydrogen chloride were formed. It can be seen by examining the equations representing the actions occurring when free chlorine bleaches and when the chlorine of hypochlorous acid bleaches, that the same amount of chlorine from the hypochlorous acid or from the



hypochlorite, has twice the bleaching power that free chlorine has; that is, if the amount of free oxygen is taken as a measure.



Hypochlorous acid and hypochlorites are therefore very active oxidizing agents, since they readily give up their oxygen, as has just been pointed out.

**Chlorine Dioxide.** — The only other known oxide of chlorine is chlorine dioxide ( $\text{ClO}_2$ ), or its double ( $\text{Cl}_2\text{O}_4$ ). Until recently, chlorine trioxide was supposed to exist. This oxide ( $\text{ClO}_3$ ) is so unstable that its experimental study is omitted.

**Physical and Chemical Properties.** — Chlorine dioxide is a gas, dark yellow in color, and easily condensed to a liquid at temperatures below  $9^\circ$ . Its density is 33.64. It is soluble in water or, better, in dilute potassium hydroxide, forming an acid solution containing two acids, chlorous and chloric, or their salts, if the gas is dissolved in potassium hydroxide.

The gas gives up its oxygen to oxidizable substances with explosive violence; *e.g.* in the case of phosphorus described under the study of Chloric Acid.

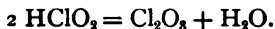
The density of the gas taken in connection with its quantitative analysis shows that the formula is  $\text{ClO}_2$ .

**Chlorous Oxide and its Corresponding Acid.** — This oxide is now said not to exist. The methods formerly used for preparation have been found to yield chlorine dioxide and free chlorine, and what was supposed to be trioxide is a mixture of these two gases.

Chlorous acid ( $\text{HClO}_2$ ) has not been prepared except in the water solution, but its salts, the chlorites, have been made. These salts are very unstable, and are therefore very powerful bleaching and oxidizing agents. (Why?) The acid is so unstable that when the base is removed from one of its salts

by such an acid as sulphuric acid, it breaks up, instead of taking hydrogen in place of the base, as is the case with many other salts and their corresponding acids.

The formula for the potassium salts is  $\text{KClO}_2$ , or  $\text{KO}-\text{ClO}$ , corresponding to the acid  $\text{HClO}_2$ , or  $\text{HO}-\text{ClO}$ . The anhydride of this acid is  $\text{Cl}_2\text{O}_3$ , according to the reaction —



**Chloric Oxide and its Corresponding Acid.** — Chloric oxide ( $\text{Cl}_2\text{O}_3$ ) does not exist, but it is the anhydride of chloric acid, which can be prepared.

**Preparation of Chloric Acid.** — Pass chlorine gas into 50 cc. of a concentrated hot solution of potassium hydroxide (2 parts of water to 1 part of potassium hydroxide) as long as the gas is absorbed. Boil the solution to remove any excess of chlorine, and also to further concentrate it. Filter, if necessary, and allow the solution to cool. Separate the crystals that form, recrystallize, and compare the crystals with known potassium chlorate. The solution from which the potassium chlorate crystals were taken should now be further evaporated and a new crop of crystals produced. Examine these latter crystals in the same way that the first ones are studied, according to the next experimental study.

**Experimental Study, No. 57.** — (a) Place two or three of the crystals first prepared in a test-tube and add a few drops of concentrated sulphuric acid, and warm carefully. Note the escaping gas and the detonations. Examine a crystal of known potassium chlorate in the same way. Does the escaping gas resemble chlorine in color? Is it chlorine?

(b) In a dry test-tube heat a few of the dry crystals and examine the escaping gas for oxygen. What is the source of the oxygen? What was the method used for its preparation? Save the contents of the tube and examine it for a chloride, as previously described,

(c) Powder a few crystals of potassium chlorate and carefully mix it with about an equal bulk of powdered cane sugar. Place the mixture on the plate of the retort-stand and drop on it a few drops of sulphuric acid. What does the residue appear to be? Sugar has the formula  $C_{12}H_{22}O_{11}$ . What does the sulphuric acid do? What is the residue? What has become of the hydrogen of the sugar? Why did the carbon disappear? Boil some of the residue in water and test the solution with silver-nitrate solution. Explain.

(d) To a solution of pure potassium chlorate add a few drops of silver nitrate and note the result. Treat a solution of the second crop of crystals in the same way. What does this result show in reference to what the residue is?

(e) Put in a conical test-glass (a short test-tube will answer) three-fourths full of water, four or five large crystals of potassium chlorate. When they have settled into the small part of the test-glass, drop in two or three small bits of phosphorus, causing them to be placed on top of the chlorate. Next, partly fill a pipette with sulphuric acid, and keeping the finger in place, put the lower end of the pipette in contact with the chlorate. Now allow a little of the acid to escape in the usual way. To what is the flash of light due? What becomes of the phosphorus? What does the sulphuric acid do?

(f) Add to 10 cc. of a water solution of potassium sulphite 5 cc. of a solution of potassium chlorate ( $KClO_3$ ). Now add hydrochloric acid. Warm the mixture and prove whether there is sulphuric acid or a sulphate present. What does it mean if a sulphate is formed? What effect does the hydrogen chloride have on the mixture?

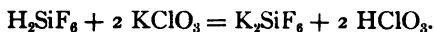
**Properties of Chloric Acid and its Salts.** — When chlorine gas is passed through a hot solution of potassium hydroxide, a different reaction occurs from that which is produced when the solution is cold. If the hydroxide solution is concentrated, there appears, on cooling, crystals, tabular in form, and perfectly

permanent in the air. Further concentration and cooling of the solution, after these crystals have been removed, develops other crystals. These are cubical in form, and when a solution of them is treated with silver nitrate, a white precipitate is formed, showing that a chloride — that is, potassium chloride — is present. The reaction is represented as follows : —

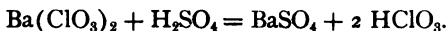


The first compound indicated in the products of the reaction has been purified, and its composition studied carefully. The formula has been determined to be  $\text{KClO}_3$ . There is but one compound formed with potassium or sodium, or any monobasic metal, and the conclusion is that the acid has but one atom of hydrogen, and this fact, taken in connection with its percentage composition, determines its formula to be  $\text{HClO}_3$ . (Explain this.)

When a solution of this compound ( $\text{KClO}_3$ ) is treated with hydro-fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), they react thus : —



Or the barium salt of chloric acid may be treated with very dilute sulphuric acid.



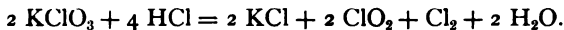
In both reactions one of the products is insoluble in water, and may therefore be removed by filtering. There remains a dilute solution of the chloric acid ( $\text{HClO}_3$ ) which may be concentrated in a vacuum, over sulphuric acid.

The acid decomposes very readily and is a powerful oxidizer. It will ignite many combustible substances by merely placing them in a concentrated solution of the acid, which is a solution containing about 40 per cent of the acid. Such substances as dry wood, paper, etc., burn rapidly. At about  $40^\circ$  the concentrated acid solution decomposes, forming oxygen, water, and

perchloric acid, the latter compound having the formula  $\text{HClO}_4$ .

Upon bases it acts like hydrogen chloride ; that is, it forms water and a salt corresponding to the acid.

The characteristic property of chloric acid and its salts is that of furnishing oxygen readily to other substances under the influence of heat. When heated to a high temperature, its potassium salt yields oxygen and potassium chloride. Concentrated sulphuric acid decomposes the chlorate, forming the gaseous compound  $\text{ClO}_2$ . Hydrochloric acid decomposes the chlorate, producing chlorine dioxide and free chlorine. The dioxide decomposes into oxygen and free chlorine by warming slightly.



When sugar and potassium are mixed and sulphuric acid is added, the chlorine dioxide which is formed oxidizes in part, at least, the carbon and hydrogen of the sugar, producing rapid combustion. It is the chlorine dioxide that oxidizes phosphorus under water when in contact with sulphuric acid.

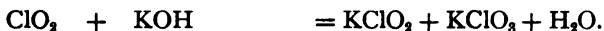
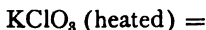
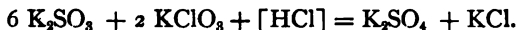
The anhydride of chloric acid is  $\text{Cl}_2\text{O}_5$ .



**Perchloric Acid and its Anhydride.** — When potassium chlorate is heated to fusion it becomes a nearly colorless liquid which gradually gives up its oxygen. If this mass be kept at about constant temperature, — that is, the temperature of fusion, — the liquid becomes pasty. If now it be cooled and examined, it will be found to contain potassium chloride, probably some undecomposed potassium chlorate, and a third substance to which the formula  $\text{KClO}_4$  has been given. When this compound is treated with sulphuric acid, there can be distilled a liquid which is nearly colorless and which possesses acid properties.

The acid thus prepared is nearly pure. It is more stable under the influence of heat than any other oxygen acid of chlorine. In general, it has the same properties as the other oxygen acids of chlorine. It is a monobasic acid, having the formula  $\text{HClO}_4$ . This corresponds to the anhydride  $\text{Cl}_2\text{O}_7$ .

#### REACTIONS.



Balance, and explain each of the reactions just indicated.

#### *Compounds of Bromine with Oxygen and Hydrogen.*

No oxides of bromine are known. Compounds of oxygen and hydrogen and bromine, or acid compounds, have been prepared. They resemble the oxygen compounds of chlorine in properties and composition.

**Hypobromous Acid and its Salts.** — This acid is formed by the action of bromine on mercuric oxide in the same manner as was the corresponding acid of chlorine. It bleaches and is an active oxidizing agent.

Its formula has been determined to be  $\text{H}-\text{O}-\text{Br}$  or  $\text{HBrO}$ . The potassium and sodium salts are formed by treating a cold solution of the hydroxides of these bases with free bromine.

The only other oxyacid of bromine that has been prepared is bromic acid, corresponding to chloric acid. Its alkali salts are prepared in the same manner as were the chlorates. Its formula is  $\text{HBrO}_3$ .

*Compounds of Iodine with Oxygen and Hydrogen.*

Only one oxide of iodine is known, and that is the pentoxide ( $I_2O_5$ ). This oxide dissolves in water, forming iodic acid. This oxide is in fact prepared from iodic acid by heating the latter to  $170^\circ$ , when a molecule of water escapes and the solid crystalline pentoxide is left.

**Oxyacids of Iodine.**—Two oxyacids of iodine are known with a number of their corresponding salts. The acids are iodic ( $HIO_3$ ) and periodic acids ( $HIO_4 \cdot 2 H_2O$ , ( $H_5IO_6$ )).

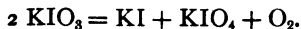
Iodic acid can be prepared by the oxidation of iodine by concentrated nitric acid.



When this method is used for the preparation of the acid, the iodine is dissolved in the concentrated nitric acid and the solution evaporated until all the excess of nitric acid is expelled. When this residue is dissolved in water, the acid may be obtained by recrystallization in the form of rhombic crystals. These crystals lose water at  $170^\circ$  and become the pentoxide ( $I_2O_5$ ).

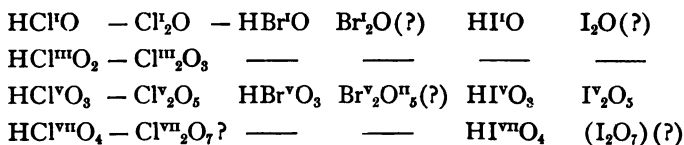
When iodine is dissolved in an alkaline solution, there are formed both the iodide and the iodate of the base used. The iodate may be separated from the iodide by the use of alcohol, since it does not dissolve in this medium, while the iodide does. The acid and its salts are very active oxidizers. The acid, its anhydride, and its salts, are more stable than the corresponding compounds of bromine and chlorine. The anhydride is decomposed at temperatures above  $300^\circ$ .

**Periodic Acid and its Salts.**—Periodic acid has not been obtained as a free acid, but its salts, like potassium periodate, are readily prepared from the iodate by means of heat.



The acid corresponding to this salt may be represented by the formula  $\text{HO} - \text{IO}_3$ . Although this acid has not been separated from its water solution, the so-called hydrates have been formed and studied. They are represented by the following formulæ:  $\text{HIO}_4 \cdot \text{H}_2\text{O}$  and  $\text{HIO}_4 \cdot 2 \text{H}_2\text{O}$ , or  $\text{IO}_2(\text{OH})_3$ , or  $\text{H}_3\text{IO}_5$  and  $\text{IO}(\text{OH})_5$ , or  $\text{H}_5\text{IO}_6$ . These compounds are crystalline solids. They are broken up by heat into water, oxygen, and pentoxide of iodine,  $\text{I}_2\text{O}_5$ . These acids are called metaperiodic acids, and the salts metaperiodates. Examples of their salts are  $\text{Zn}_3(\text{IO}_5)_2$  and  $\text{Na}_3\text{IO}_6$ .

**Valence of the Halogen Group.** — The valence of the halogens for hydrogen is unity. An examination of the compounds formed with oxygen shows that these elements have a variable valence towards the former. The acids and their corresponding oxides or anhydrides are the following: —



Most of these anhydrides have not been separated from their corresponding acids, but a study of these compounds and their acids shows that the valence of this group varies from 1 to 7, or is 1, 3, 5, and 7.

### *Compounds of Carbon with Oxygen, and with Oxygen and Hydrogen.*

**General Consideration.** — There is no element that forms such a number and variety of compounds as does the element carbon. It forms an essential part of every substance that owes its formation to life, whether of animal or of vegetable origin. The number of compounds formed with hydrogen alone is



legion, but in all the cases that have been studied, their composition has been explained on the basis that carbon is tetrivalent, as it was shown to be in marsh gas or methane. The number of the carbon compounds containing either carbon and hydrogen alone, or these two elements along with oxygen and nitrogen, one or both of them, is so large that they are usually studied by themselves under the title of organic chemistry. These organic compounds were formerly supposed to differ from inorganic compounds in that they could only be produced under the influence, or control, of life, or the vital forces. In 1828 one of the simplest organic compounds, urea, was prepared by Wöhler. Since then, the number of organic substances prepared in the chemical laboratory has come to include a large per cent of all that nature produces. Each year sees some of the compounds not previously produced artificially, added to the list of those thus prepared. It would lead the student too far from the purposes of this work to discuss further the so-called organic compounds. Consequently only the simple compounds of carbon will be here studied.

### *Oxides of Carbon.*

#### (a) CARBON DIOXIDE.

**Preparation from the Elements.** — Fill a 200 cc. gas bottle with oxygen gas and place in it, by means of the iron spoon, a piece of carbon (charcoal), at ordinary temperatures at first, following it by gradually increasing temperatures until it ignites. Note the temperature of ignition. Prepare several bottles of gas in this way. Of what must the compound be composed?

**Experimental Study, No. 58.** — (a) Add to one of the bottles 10 cc. of lime-water, or, better, 10 cc. of barium hydroxide solution ( $\text{Ba}(\text{OH})_2$ ). Close the bottle and shake

well. Remove the water and the precipitate to a test-tube. Boil, and allow the precipitate to settle. Decant off the liquid, and treat the solid residue with a drop of hydrochloric acid. What escapes? The formation of this precipitate under these conditions is a characteristic test for this compound.

(*b*) Recall and note all the other gaseous compounds studied. They do not form precipitates with either of the reagents, calcium or barium hydroxide.

**Preparation of the Compound from Other Compounds.** — **Carbonates.** — Place in a generating bottle 20 g. of powdered marble (ordinary limestone will answer) and prepare for collecting gas over water or by downward displacement. Pour down a thistle-tube about 20 cc. of hydrochloric acid. Collect the escaping gas over water, after rejecting the first bottle of gas.

**Experimental Study, No. 59.** — (*a*) Pass some of the gas into lime-water. Is the gas the same as that produced by the union of carbon and oxygen; that is, is it so as determined by this test?

(*b*) Examine the gas for its physical properties. Its mass relation to air may be determined by placing a bottle of air and gas mouth to mouth. Bring them to a vertical position with the carbon dioxide bottle uppermost. Test each jar after a minute or two with a burning stick.

Also place a lighted candle on the table and hold a bottle of the gas over it, as if pouring from it on the flame.

(*c*) Test the gas with a burning stick and explain the result. What does the stick supply to the chemical action?

(*d*) Test the water solution of the gas with litmus, or pass the gas through a dilute solution of litmus for a few minutes.

(*e*) Test a bottle of the gas with magnesium wire at ordinary temperatures, and also when the wire is ignited. The wire should be carefully scraped to remove the oxide that adheres to its surface. What are the deposits? Source of each.

(*f*) Fill a dry bottle or tube with the gas and place in it a small piece of sodium, and warm gently. Note the residue in (*e*) and (*f*). What is it? What change has the magnesium and sodium produced? Have they produced the same results. Explain fully.

(*g*) Use sulphur in the same manner as the magnesium wire was used.

(*h*) Pass the pure gas into a test-tube one-half full of potassium hydroxide solution. Notice the action on the bubbles of gas as they ascend through the liquid. Continue to pass the gas as long as it is absorbed. Transfer the contents of the tube to an evaporating-dish and evaporate to dryness. Examine a portion of the residue with an acid.

(*i*) Pass the gas into a solution of barium chloride; the same for a solution of magnesium sulphate. Is there any precipitate formed? Treat the same solutions with a solution of sodium carbonate.

(*j*) Breathe through a solution of lime-water, using a small glass tube to convey the breath. What does the result indicate? Allow the precipitate to settle; pour off the clear liquid and treat the residue with hydrochloric acid. Explain.

(*k*) Lower a burning candle into a bottle of air and test the product with lime-water in the usual way. Explain.

(*l*) Heat a metallic oxide, like copper oxide, which has been thoroughly mixed with carbon in a dry tube, and pass the gas into lime-water. This result typifies the action of carbon with most metallic oxides. What is the solid residue?

(*m*) Saturate water with carbon dioxide. Fill a large test-tube with this water and place in it the leaves of a growing plant like peppermint, or, better, a water-plant, like the chara. Invert the tube in a dish containing the saturated water, and place the whole in the direct sunlight for several hours. Examine the gas that collects in the tube. Test it with a burning match.

(*n*) Pass the gas slowly through lime-water for half an hour. Notice what changes occur in the precipitate that is first formed. Boil 20 cc. of the solution for some minutes. Is there any increase in the precipitate? From whence does it come? Treat a portion of the clear solution with a dilute solution of soap. Pour off the clear liquid from the solution that has been boiled and treat it with some of the soap solution. Compare these results with those produced by putting soap into so-called hard water.

(*o*) Prepare a solution of sugar (5 to 10 per cent), placing 75 cc. of it in a 100 cc. flask, and add to it some ordinary yeast. Fit up the flask to collect gas, and place the end of the collecting tube in 20 cc. of lime-water. Place the whole in a warm place and allow it to stand for at least 24 hours. What gas escapes? (Pasteur's fermenting solution may with advantage take the place of the sugar solution. See Huxley and Martin's Biology, p. 6.)

**Composition and Formula of the Gas.**—Use the apparatus shown in Fig. 10. This is the same apparatus as that used in studying sulphur dioxide. Place in the spoon attached to the stopper a piece of carbon (diamond or charcoal). If the charcoal is used, it must be heated to redness away from the air, to remove any possible undecomposed carbon compounds. It is best to prepare charcoal from pure sugar for this study. Fill the apparatus with pure oxygen gas (over mercury). The volume of the oxygen is to be noted. Properly connect the apparatus with the electric battery and pass the sparks until the carbon is ignited, allowing the action to continue until all the oxygen has combined with the carbon. The apparatus is allowed to cool to the temperature it had at the beginning of the experiment, when the volume of the gas will be found to be the same as the original volume of the oxygen.

How much oxygen by mass enters into 100 cc. of the gas,

according to the above facts? What is the per cent of oxygen in the compound?

The amount of carbon in the oxide is determined by oxidizing a known weight of the carbon, and then weighing the product.

A hard glass tube, containing a weighed amount of pure carbon (diamond or sugar carbon) is placed in an ordinary combustion furnace and connected at one end with a supply of pure oxygen. To the other end of the tube are connected absorption tubes, containing potassium hydroxide, to absorb the oxide of carbon as fast as it is formed. The exact mass of this tube or tubes is known. Precautions must be taken to have the oxygen gas perfectly dry, and also to remove and absorb any moisture that may be in the copper oxide that is placed in the tube in front of the carbon. Explain the use of each of the substances that have been mentioned as used in this examination.

Calculate the per cent of carbon in the oxide from the following facts: The average of ten determinations, such as have been described, showed that .5 g. of carbon formed 1.833 g. of the oxide.

**Facts.** — (a) From the quantitative analysis of the compound the percentage composition is carbon 27.27, and oxygen 72.73 per cent.

(b) The density of the gas is 21.945.

(c) The atomic masses of the elements are known.

(d) One volume of the gas contains one volume of oxygen.

**Problem.** — From the facts just given show why the formula for the compound is  $\text{CO}_2$ .

**Physical Properties.** — Carbon dioxide is a heavy, colorless gas. Its specific gravity on the air scale is 1.52, and on the hydrogen scale it is 21.945. When the gas is subjected to pressure at a temperature below  $30.9^\circ$ , it can be converted into a liquid. This liquid may be changed to a solid by removing the pressure and allowing the gas to escape into the air.

The energy required to convert a portion of the liquid into a gas is furnished by the remainder of the liquid, which is thus cooled to a solid condition much resembling snow in its general appearance. The liquid carbon dioxide boils at  $-78^{\circ}$  under one atmosphere of pressure. The gas is soluble in water, the amount varying with the temperature of the water and the pressure to which it is subjected. At ordinary temperatures 1 vol. of water absorbs an equal volume of carbon dioxide. At  $0^{\circ}$  1 vol. of water dissolves 1.79 vols. of gas. The gas is absorbed according to Dalton and Henry's law. Thus, under ordinary temperature and pressure, 1 vol. of water absorbs 1 vol. of gas; under double the pressure, 2 vols. of gas are absorbed, measured at the unit of pressure or the same volume measured under the double pressure, and so on for higher pressures, the temperature being constant. Use is made of this fact in preparing effervescing liquids such as beer, champagne, soda water, etc. Water, or these liquids, which are largely composed of water, is made to absorb carbon dioxide under pressure, and when the pressure is removed, the gas escapes. (What is the foam on the top of a glass of soda water?) The name *soda water* originated from the fact that bicarbonate of sodium is, or was, used to furnish the carbon dioxide for the charging of the liquid.

**Chemical Properties.** — The water solution of carbon dioxide is slightly acid to litmus, especially after standing some time, indicating that this oxide acts towards water like the other non-metallic oxides. However, when the solution is heated to expel the excess of water, the carbon dioxide escapes, showing that the compound is an unstable one. If a water solution of the gas is treated with bases, or the gas is passed into a solution of bases, such as potassium hydroxide or calcium hydroxide (lime-water), stable compounds are formed. A study of these compounds leads to the supposition that the acid formed has the formula  $\text{H}_2\text{CO}_3$ , since there are two salts of each

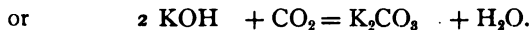
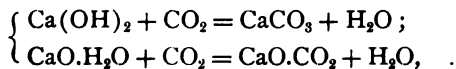
sodium and potassium, one containing hydrogen, sodium (or potassium), carbon, and oxygen, and one containing no hydrogen and two equivalents of sodium (or potassium), and no hydrogen. These salts are very stable compounds, and the quantitative analysis of these compounds shows that for every two equivalents of the metals mentioned there are 12 parts of carbon and 48 parts of oxygen.

The carbon in this gas is held by the oxygen at ordinary temperatures with great tenacity. It is decomposed by but few substances except at very high temperatures. Magnesium and the alkaline metals will decompose it at moderately high temperature, the carbon being set free, the oxygen uniting with the metals. The gas is produced when metallic oxides are heated with carbon.

**Carbonates.** — Carbonic acid is a dibasic acid and consequently forms two classes of salts — the acid and normal ; for example,  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$ . It is thus shown to contain two atoms of hydrogen. These carbonates are readily decomposed by acids ; a salt corresponding to the acid used is formed, and carbon dioxide and water are set free. In the preparation of the gas from limestone this reaction occurs : —

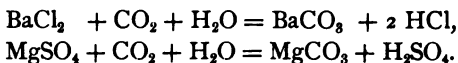


Carbonates are formed by the action of carbon dioxide on bases thus : —



The carbonates are all insoluble in water except those formed with the alkali bases. When the gas is passed into solutions of the salts of other acids, *e.g.* barium chloride ( $\text{BaCl}_2$ ) or of

magnesium sulphate ( $\text{MgSO}_4$ ), the following reactions may be regarded as occurring at first : —



These salts are insoluble in water, but the acid set free will decompose them if formed, in the same way that the calcium carbonate was decomposed in preparing carbon dioxide. If ammonium hydroxide is added, it unites with the acid, forming its corresponding salt, and the insoluble carbonate is formed.

**Tests for Carbon Dioxide and Carbonates.** — The free gas is distinguished from other gases by its action on calcium or barium hydroxides, forming the insoluble calcium or barium carbonate. The carbonates are decomposed by acid effervescing rapidly with the stronger acids. The escaping gas is recognized by the calcium hydroxide test and by its physical properties.

**Occurrence of Carbon Dioxide.** — This gas is present in the atmosphere in varying quantities, the average being about 3 vols. of the gas in 10,000 vols. of the air. Carbon dioxide being the product of the oxidation of the carbon of ordinary fuel, it being also a product of animal respiration, and of the decay of organic matter, it is always found in the atmosphere. It is found in natural waters, especially in mineral springs, giving to the water a sparkling appearance and an agreeable taste. It escapes from the earth in large quantities in volcanic regions, and is often found in mines and caves, and is there known as choke-damp. It occurs in large quantities in combination in carbonates. (See under the various metallic carbonates.)

**Relation of Carbon Dioxide to Life.** — It has been shown that carbon dioxide is a product of animal respiration. A portion of the oxygen that is inhaled unites with some of the carbon of the organic compounds with which it comes in



contact in the body, forming the dioxide, and is then exhaled as a part of the breath. It is thus seen that animals are constantly locking up, as it were, the oxygen of the world in a very stable compound, and in time it might be expected that all of the oxygen of the air would be exhausted. This seems more evident when all the other methods of removing oxygen from the air are considered; as for example, by the combustion of fuel, the decay of animal and vegetable matter. However, so far as accurate observations have been made, no diminution in the amount of oxygen in the air has been discovered. Many facts go to show that there has been no appreciable loss of oxygen.

This gas which is thus being constantly supplied to the air is one of the chief foods of the plant world. It is taken up by the plants, and in connection with sunlight it decomposes it, setting the oxygen free, which thus becomes a part of the air again. The carbon becomes, through the agency of plant life, a part of the various complex vegetable compounds which serve as food for animals, or fuel for our fires, etc. This decomposition of carbon dioxide and the subsequent construction of its carbon into such compounds as starch, cellulose, etc., is done in the chlorophyll cells of the plant. These compounds are oxidized again, and the round of changes is repeated. The heat energy given out in this oxidation, whether done in the animal body or in the atmosphere, was supplied by the sun. If the plant is not placed in the sunlight, it has no power to construct these complex substances, and as an individual it dies. The heat, therefore, that is supplied to the animal body has its source in the sun. Or again, when heat energy is used in running machinery by means of the energy furnished through the steam engine, the source of this energy is directly traceable to the sun acting to produce the plant, which yields it up when it is oxidized under the boiler. Notice that not only is the carbon built into the various compounds, but the oxygen is set

free at the same time, by the same power, and thus prepared for the processes of oxidation.

**Effect of Carbon Dioxide on Life.** — Carbon dioxide is not an active poison. The gas is always present in the lungs of man, for example, and as has been seen, it is present in the ordinary air. The pure gas produces death when inhaled by shutting out the oxygen and thus depriving the body of its essential element, and suffocation follows.

When the amount of carbon dioxide in the air we breathe reaches 4 to 5 per cent, it produces detrimental effects, largely because it so dilutes the air that the supply of oxygen is not sufficient. Even 1 to 2 per cent of the gas produces depression and headache if inhaled for a long time.

Every breath of air exhaled from the lungs of a man gains about 4 per cent, by volume, of carbon dioxide and has lost about 5 per cent of oxygen; that is, if the air has been breathed but once. Therefore, the inhalation of this air for a second time will be injurious, and if continued, will produce death. A single person exhales about 20,000 cc. of carbon dioxide per hour, and absorbs about 25,000 cc. of oxygen. Now, in order that the exhaled air may be breathed again, it should be mixed with at least 32,000 l. of pure air, requiring a space of about 1.7 m. in each of its dimensions. If the gas produced by a burning lamp, gas-jet, etc., be taken into account, the necessity of frequent changes of the air in living-rooms becomes evident. It is also true that in addition to the carbon dioxide given off by the lungs in respiration, there are organic substances given out that are perhaps more injurious to life than is the carbon dioxide. These substances rapidly undergo decomposition in the air, producing poisonous compounds. These substances must be removed from living-rooms by currents of air passing out of the rooms, since they do not obey the ordinary laws of the diffusion of gases.

**“Hard” Waters and Carbonates.** — As has been stated,

all the normal carbonates, excepting those of the alkalis, are insoluble in water; but if the water is charged with carbon dioxide, many of them are dissolved in quite large quantities. It is claimed that acid carbonates are formed which are soluble in water; *e.g.* calcium carbonate is so insoluble in water that only about 18 mg. are dissolved in a litre of it, but when the water contains carbon dioxide a much greater amount goes in solution. (See under CALCIUM CARBONATE.) When this solution is boiled, carbon dioxide escapes, and the excess of the carbonate over the amount just stated is deposited.

When such water is treated before boiling with a soap solution, a solid compound is formed with a portion of the salt, thus actually destroying a portion of the soap. When the water has been boiled, the amount of the compound formed with the salt is quite small. Waters holding this excess of carbonate in solution are called "hard" waters.

These carbonates are deposited on the sides and bottoms of kettles, boilers, and other vessels in which such waters have been boiled.

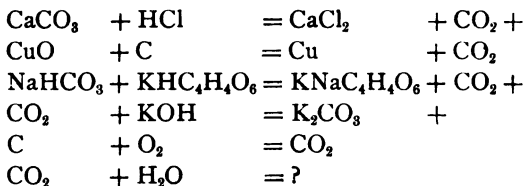
**History and Name.** — Carbon dioxide was first described as "chalky air," since it was produced from chalk or limestone, to distinguish it from the ordinary air. Attention was called to the gas by Paracelsus, who claimed that it was a different substance from the air. It was soon after examined by other students of nature, especially by Van Helmont, who showed that it might be prepared in several ways. For example, by the fermentation of sugar solutions, by the action of acids on marble, by the oxidation of carbon, etc.

In 1775 Lavoisier determined its composition, and that it is an oxide of carbon.

**Tests.** — Carbon dioxide produces a white precipitate of calcium carbonate ( $\text{CaCO}_3$ ) when passed into a solution of calcium hydroxide ( $\text{Ca(OH)}_2$ ) or lime-water. In general, this is the only gas which produces this result, and hence it is a characteristic test for the substance.

**Uses.** — Carbon dioxide has many useful applications in the arts and manufactures. It is employed by all civilized peoples to render bread "light." The source of the gas is commonly the fermentation of sugar solutions by the yeast plant, the yeast being added to the dough. It may also be produced by mixing into the flour, before it has been wet, a carbonate and some solid acid, or acid salt. The acid carbonate of sodium ( $\text{NaHCO}_3$ ) and tartaric acid or its acid salts ( $\text{KHC}_4\text{H}_4\text{O}_6$ ) are most generally used. It is used in certain kinds of fire-extinguishing apparatus, the carbon dioxide being rapidly generated around and above the burning material, thus cutting off the supply of oxygen. The gas is also used to charge water, soda water, and various kinds of effervescent liquid.

## REACTIONS.



Balance, and explain the preceding indicated reactions.

**Problem.** — How much carbon dioxide, by mass and by volume, can be obtained from 100 g. of marble, 10 per cent of which is impurities? How much hydrochloric acid will be necessary to decompose the carbonate, the acid solution containing 20 per cent of hydrogen chloride.

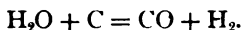
## CARBON MONOXIDE.

**Methods of Preparation.** — When a small supply of oxygen passes over red-hot carbon, the latter does not become completely oxidized to carbon dioxide, but a compound containing

one-half as much oxygen is produced. The result is also reached by passing carbon dioxide over red-hot carbon. The carbon dioxide loses one-half of its oxygen.

These methods of preparing carbon monoxide are illustrated in an ordinary base-burning, hard coal stove. The supply of air, which enters at the bottom of the stove and passes up through the mass of burning coal, soon oxidizes the carbon to carbon dioxide. The gas thus produced passes up through the hot coal along with the air, which has lost its oxygen. The dioxide divides its oxygen with some of the hot carbon, forming the monoxide. If air is supplied to the space above the coal, a blue flame appears, caused by the complete oxidation of the carbon monoxide.

The gas is also made by passing steam over white-hot carbon. Under these conditions the water gives up its oxygen, hydrogen is set free, and carbon monoxide (CO) is formed.



The compound is also prepared by decomposing such compounds as oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), formic acid ( $\text{HCO}_2\text{H}$ ), and potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ), by means of sulphuric acid.

**Preparation.** — Fill a hard glass tube 40 to 60 cm. long with finely powdered charcoa', and place it in a combustion furnace. The ends of the tube should be fitted with corks provided with glass tubes for attaching rubber tubing for the purpose of conducting gases to and from the tube. (A piece of one-half-inch iron gas-pipe answers well in place of the glass tube.) The tube is now connected to the carbon dioxide generator, filled with the gas, and heated to full red heat. Attachment is now made at the other end to the tube for collecting gas over water, and a slow current of carbon dioxide is passed through the apparatus. If the product of the reaction in the tube is

passed through a solution of potassium hydroxide, the collected gas is nearly pure carbon monoxide.

An interesting variation of this experiment is made by collecting a 4 or 5 l. rubber gas-bag, half full of carbon dioxide, and connecting it to one end of a tube prepared as just described. To the other end of the tube attach an empty bag of the same size and kind. Now force the carbon dioxide slowly through the tube into the empty bag. Pass it back and forth several times. It will be noticed that the volume of the gas increases, and that when decomposition is complete the volume is doubled.

The same apparatus may be used to show that in a small supply of oxygen carbon monoxide is produced instead of the dioxide. This is done by preparing a tube described in the first method of preparation, heating it to red heat and passing a slow current of air through it, and collecting the product in the usual manner of collecting gases. Steam may be passed through this tube, if an iron one is used, and the gaseous product will be found to consist of equal volumes of the monoxide and hydrogen.

From oxalic acid the oxide is made as follows:—

Place in a 100 cc. flask 15 g. of crystallized oxalic acid and 50 cc. of concentrated sulphuric acid. Prepare to pass the gaseous products through a solution of potassium hydroxide and collect the escaping gas as usual over water. Warm the flask, gently regulating the heat according to the flow of gas. What is the relation between carbon dioxide and potassium hydroxide? Watch the bubbles of gas as they pass through the solution. What effect does it have on the size of the bubble? Collect sufficient gas for its study.

**Experimental Study, No. 60.**—(a) Make the usual tests for solubility and other physical properties.

(b) Test a bottle of the gas with a lighted stick and note the action that occurs. Cover the bottle and test the contents with lime-water,

(*c*) Test a bottle of the gas with magnesium wire. Be sure and place the wire down into the gas, and also that the wire is rapidly burning. What are the products?

(*d*) Add to a bottle of the gas 20 cc. of a solution of cuprous chloride ( $\text{Cu}_2\text{Cl}_2$ ). Close the bottle tightly and notice and prove the absorption of the gas.

(*e*) Heat some of this last solution and prove whether the gas escapes again by passing into lime-water.

(*f*) To one-half bottle of the gas add an equal amount of air. Wrap the bottle around with a towel and ignite the mixture. What are the products? Prove what they are. What should be the volume proportion of the gas and air, CO being the formula for the gas, and carbon dioxide the product?

(*g*) In a hard glass tube 12 to 15 cm. long place 2 g. of copper oxide ( $\text{CuO}$ ). Place the tube in a horizontal position and connect it in such a manner that the products can be collected. Heat the tube opposite the oxide and pass over it carbon monoxide. Prove that the carbon dioxide is formed. Be sure that the monoxide is free from the dioxide. What is the effect upon the copper? What kind of an agent is the monoxide? Why?

(*h*) Mix equal volumes of dry chlorine gas and carbon monoxide and expose them to the sunlight. Examine the mixture, and determine whether a chemical change takes place. Add water to the bottle and shake well. To the solution add a few drops of nitric acid and silver nitrate. Explain.

(*i*) Expose a live mouse to the action of the gas by filling a jar with the gas and placing the mouse in it. Note the effect on the mouse and the time that it lives.

(*j*) Pass into eudiometer tube, over mercury, a definite volume of carbon monoxide (say 10 cc.) and 8 cc. of pure oxygen. Pass the electric spark, and after the temperature has been adjusted to that which the original gas had, note the volume of the product. What is it? Pass into the tube a piece

of moist potassium hydroxide. What will it absorb? Prove what the remaining gas is and what its volume is.

**Determination of the Composition and Formula of this Carbon Compound.** — In (*j*) there were taken 18 cc. of mixed gases, 10 cc. of the carbon monoxide, and 8 cc. of oxygen. After the passage of the electric spark and the exposure of the gaseous products to the action of potassium hydroxide, there remain 3 cc. of pure oxygen, showing that the 10 cc. of the gas united with 5 cc. of oxygen. The volume of the product was also shown to be twice the volume of the original gas. The product was proved to be carbon dioxide.

From these facts determine (*a*) that the percentage composition of the compound is 42.853 per cent for carbon, and 57.147 per cent for the oxygen. What was the mass of the original gas, its density being 13.965? What was the mass of the oxygen added? What was the weight of the product? How much carbon, by mass, was there in this carbon dioxide? Therefore, how much carbon was there in the original gas?

(*b*) Determine that the formula should be CO, from the facts just given, the atomic mass of the elements of the compound being known.

**Physical Properties of Carbon Monoxide.** — Carbon monoxide is a gas possessing a somewhat characteristic odor, no taste, and no color. It is not soluble in water. The gas has the density of 13.965, and can be condensed into a liquid at a temperature of  $-190^{\circ}$  under 760 mm. pressure. When this liquid is placed in a vacuum, it is converted into a solid by its own evaporation, producing a temperature of  $-210^{\circ}$ .

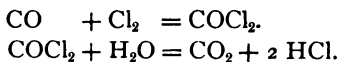
**Chemical Properties.** — The most remarkable characteristic property of this gas is the readiness with which it takes oxygen to form carbon dioxide at high temperatures. It forms explosive mixtures with the air, and removes oxygen from such metallic oxides as copper, zinc, and iron. This property makes it useful in the manufacture of iron. (See under IRON.) Its



union with oxygen is accompanied by the evolution of much heat. When carbon unites with oxygen to form carbon dioxide, 96,960 calories of heat are given out; that is, when 12 g. of carbon unites with 32 g. of oxygen. When 12 g. of carbon and 16 g. of oxygen unite to form carbon monoxide, only 28,590 calories of heat are liberated, thus making the heat of formation of carbon dioxide, when produced from carbon monoxide and oxygen, 68,370 calories. It will be noticed that this latter heat of formation is more than twice larger than that evolved in the formation of carbon monoxide.

**Water Gas.** — Water gas is a mixture of carbon monoxide and hydrogen, produced by the action of very hot carbon on water when it is in the form of steam. When this mixture is oxidized again, a large amount of heat is given out, as has just been indicated. Because of this fact the mixture is used for heating purposes. It oxidizes with a colorless flame. When this mixture is further mixed with gases rich in carbon, the flame becomes colored, when the gas is oxidized and is suitable for illuminating purposes. This mixture is called water gas. It is made from anthracite coal or from coke, by passing steam into chambers in which coal or coke is heated to a bright red temperature.

Carbon monoxide unites with chlorine gas when a mixture of the two gases is exposed to direct sunlight. Equal volumes of the gases unite, forming a gaseous product called carbonyl chloride, and to which the formula  $\text{COCl}_2$  has been given. The volume of the product is one-half the combined volumes of the gases that enter into the reaction. The compound may be regarded as carbon dioxide, in which one atom of oxygen has been replaced by two atoms of chlorine. When the gas is passed into water, it is decomposed, and hydrogen chloride and carbon dioxide are formed.



Carbonyl chloride is used in making some of the valuable aniline dyes.

Carbon monoxide is an active poison, especially when it is inhaled. Very small quantities of the gas produce headache, and finally insensibility. It is therefore a dangerous substance; and since its odor is so slight, it is not easily detected. It is said to pass through red-hot iron, and thus contaminate the air of living-rooms where anthracite coal stoves are heated to high temperatures. In case the draught of a chimney is weak the gas frequently escapes from ordinary coal stoves. When used as a part of illuminating gas, great care is required in selecting pipes in which to convey it and in making the unions gas-tight.

It is said that 1 vol. of the gas in 100 vols. of air renders the mixture unfit to breathe. The monoxide unites with the hæmoglobin of the blood, forming a chemical compound with it, and setting free an equal volume of oxygen, thus depriving the blood of its available oxygen.

**History and Name.** — This oxide has been variously named. For example, it has been named carbonic oxide, carbonous oxide, carbonyl, and more recently carbon monoxide.

The substance was discovered in 1776 by Lassone, and later (in 1796) by Priestley. In the year 1800 its composition was determined by several chemists.

**Uses and Tests.** — Carbon monoxide is detected by its oxidation in air, producing a blue flame, together with the fact of the formation of carbon dioxide as a result of this oxidation. It is interesting to note here that the dry monoxide does not unite with perfectly dry oxygen even at high temperatures.

Carbon monoxide is a very useful substance; in fact, it is a necessary substance in the preparation of iron and in many other metallurgical processes. In these processes of extracting metals, the monoxide at the high temperature of the furnace takes the oxygen from the metal, setting the latter free, and becoming carbon dioxide itself.

*Compound of Carbon with Sulphur.*

**Preparation.** — There is but one compound of sulphur and carbon known, and this one is not found in nature. This compound serves many important uses and is manufactured on a large scale. It is prepared by the direct union of carbon and sulphur. It has been noticed already that sulphur replaces oxygen in many compounds, but that these compounds are not so readily formed, nor are they as stable when formed as are the oxygen compounds. The union of sulphur takes place when the carbon is red-hot, at which temperature, of course, the sulphur is in the form of vapor. There is this difference between the union of sulphur and carbon and the union of carbon and oxygen: the temperature of ignition is quite high in the latter case, but when once begun, the heat produced by the union is sufficient to continue the action; but in case of the union of sulphur and carbon, heat must be continually supplied or the action ceases. In the experimental study of the compound its preparation will be omitted, but the compound should be examined as follows: —

**Experimental Study, No. 61.** — (a) Pour a few drops of the sulphide of carbon on the hand, and notice its volatility and odor. Note its other physical properties.

(b) Place 1 cc. of the liquid in a dry gas bottle; cover loosely, and shake. Now bring a glass rod heated as hot as a Bunsen lamp can heat it, into the vapor. What are the conditions here? What substances are present? What products should you expect? Why is there any sulphur deposited on the sides of the bottle? Suppose the bottle has been full of oxygen at the start, would the result have been different? Prove what the products are.

(c) Compare the ignition temperature of the gas at the table with that of carbon disulphide. What does the ignition mean in this case?

(*d*) Treat a solution of lead acetate with a few drops of the disulphide and shake thoroughly. Compare with the action of hydrogen sulphide on the same solution. (See under HYDROGEN SULPHIDE.) Is there any apparent difference in the way the sulphur is combined in the two cases?

(*e*) (Great care should be used in performing this experiment.) Place 5 to 10 cc. of carbon disulphide in a test-tube or in a small "E" flask fitted up to collect gas. Place a jet for oxidizing gas in the end of the collecting tube. Place the test-tube or flask in boiling hot water, and when sufficient gas has escaped to permit the lighting of it without explosion, ignite it, and bring into the flame some fine iron or copper wire. Save the product, and when cold treat some of it with hydrochloric acid. What gas escapes? What is the product in the first case? Hold in the flame a crystal of copper sulphate. (The examination should be made in a draught of air or under a hood.)

(*f*) While the vapor from the carbon disulphide is oxidizing, place the jet in a bottle of air or, better, in a bottle of oxygen. Hold the jet there as long as any chemical action continues, keeping the bottle covered. Next place 30 cc. of water in a bottle; close it, and shake thoroughly. Test portions of this solution for carbon dioxide, and another portion for sulphur dioxide. (See SULPHUR DIOXIDE.)

(*g*) Repeat the experiment with nitric oxide and carbon disulphide described under the study of nitric oxide.

(*h*) Its solvent action on fats, iodine, and resins may be tested. Recall its action on iodine, sulphur, and phosphorus.

**Physical Properties of Carbon Disulphide.** — Carbon disulphide is a very volatile liquid, boiling at  $46.5^{\circ}$ . It is so volatile that its vaporization produces quite a low degree of temperature. Ice may be produced when it is rapidly evaporated from a thin-walled vessel which is surrounded by water. The water is soon congealed. The odor of the pure compound

quite resembles that of chloroform. The unpleasant odor of the commercial article is due to the presence of other compounds. It possesses a high refractive power for light, thus determining its use in refractive prisms. The density of carbon disulphide vapor is 37.95. It is insoluble in water, but mixes with alcohol, chloroform, benzole, etc., in all proportions.

**Chemical Properties.** — The vapor of carbon disulphide unites with oxygen at  $149^{\circ}$ , forming carbon dioxide and sulphur dioxide. It does not decompose metallic salts in solution, as does hydrogen sulphide and the soluble sulphides generally. At high temperatures its vapor is decomposed by many metals, forming the sulphide of the metal and setting carbon free. Iron in the oxidizing vapor takes sulphur and forms ferrous sulphide (FeS).

Carbon disulphide is poisonous when its vapor is inhaled even in small amounts; if in the latter case, the inhalation is continued for some time.

**Determination of the Formula of the Compound.** — The vapor density of carbon disulphide is 37.95; it contains 15.97 per cent of carbon and 84.21 per cent of sulphur. Show why its formula is given as  $\text{CS}_2$ .

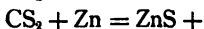
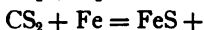
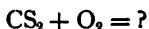
**History and Name.** — Carbon disulphide was discovered in 1796 by Lampadius, and later, in 1802, by Clément and Desormes, while studying the action of sulphur on carbon. Its composition was discovered afterwards by Vanquelin, while examining the action of the compound on metals, particularly its action on copper.

The name is formed according to the ordinary system of nomenclature.

**Uses and Tests.** — Owing to the poisonous qualities of carbon disulphide it is used to kill vermin and insects, especially those found in grain. The grain is placed in a closed chamber and there exposed to the vapor of the disulphide for a sufficiently long time to kill both the insects and their larvæ. It is then

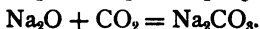
removed and the grain exposed to the air for a time, when the disulphide escapes, and if the latter is pure, it leaves the grain as pure as it was before the treatment. The compound is used as reagent in the laboratory for dissolving and recognizing iodine and bromine. The grape-vine pest of France, the phylloxera, is destroyed by the use of this substance. It is also used to dissolve gums, fats, caoutchouc, sulphur, and phosphorus. It is used to dissolve sulphur employed in vulcanizing rubber. Large quantities of the sulphide are employed to extract many of the essential oils, the oil from linseed oil cake, and in purifying wool used in the manufacture of yarn, cloth, etc.

## REACTIONS.

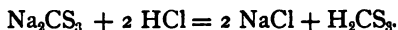


Balance and complete the equations.

**Sulphocarbonic Acid and its Salts.** — Sulphur may take the place of oxygen in carbonic acid and carbonates, forming compounds of the same general formulæ. For example, when carbon disulphide ( $\text{CS}_2$ ) is treated with a solution of sodium sulphide ( $\text{Na}_2\text{S}$ ), the following reaction occurs : —



This salt is transposed by the weaker acids, like hydrochloric, and sulphocarbonic acid is formed.



The sulphocarbonic acid, which is a brownish yellow, oily liquid, separates out as a result of this reaction. Note that

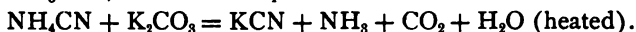
carbonic acid ( $\text{H}_2\text{CO}_3$ ) has not been separated from its water solution, and therefore that the sulphur compound is the more stable one. The acid is, however, quite readily decomposed into carbon disulphide and hydrogen sulphide.

A compound is also known corresponding to carbon dioxide, in which an atom of sulphur has replaced an atom of oxygen in the dioxide. It has the formula  $\text{COS}$ . It is a heavy gas, having a density of 30. It is formed by passing carbon monoxide through a tube containing sulphur vapor.

### *Compounds of Carbon and Nitrogen and Hydrogen.*

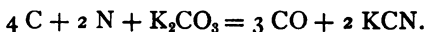
#### (a) HYDROGEN CYANIDE.

**Preparation.** — Carbon does not form compounds with nitrogen at ordinary temperatures, but when ammonia ( $\text{NH}_3$ ) is passed over red-hot carbon, two atoms of hydrogen are displaced by an atom of carbon and a volatile compound having the formula  $\text{HCN}$  is produced. This product has acid properties, and consequently unites with some of the base, ammonia, and forms ammonium cyanide ( $\text{NH}_4\text{CN}$ ). If this ammonium cyanide is treated with potassium carbonate, potassium takes the place of the ammonium, and potassium cyanide is formed.

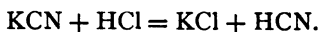


If potassium carbonate is heated to a high temperature with carbonaceous material containing nitrogen, the carbon takes the oxygen from the carbonate, and the potassium unites with the carbon and nitrogen to form potassium cyanide ( $\text{KCN}$ ), which is a solid non-volatile substance. The carbonaceous material may be bone, gelatine, hair, and like substances.

Again, it may be prepared by passing nitrogen over an intimate mixture of carbon (charcoal) and potassium carbonate ( $K_2CO_3$ ).



When the potassium cyanide formed by any of the preceding methods is treated with sulphuric or hydrochloric acid, the hydrogen cyanide is set free.



**Properties.** — The compound HCN is a volatile liquid, boiling at  $26.5^\circ$ . It may be condensed to a liquid which has a very characteristic odor, described as that of bitter almonds. It is soluble in all proportions of water, the solution presenting the same properties as the pure substance. The density of the compound is 1.3.49, and its percentage composition is hydrogen, 3.707 per cent; nitrogen, 51.93 per cent; and carbon, 44.362 per cent. (Explain the formula for the compound.)

The acid, commonly called prussic acid, is one of the most active poisons known. A single drop of the acid in the eye of a cat has produced death in thirty seconds. Four milligrammes is a fatal dose for an adult person if taken internally.

In water the acid slowly undergoes a change, ammonia being one of the compounds formed. The acid properties of this compound are very weak, so weak that its salts are decomposed by nearly every other acid, even by carbonic acid.

**Name and History.** — Hydrogen cyanide was discovered by Scheele in 1782. It was studied and its properties pointed out in connection with those of cyanogen by Gay-Lussac about 1815.

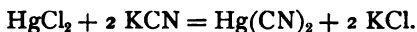
It was at first called prussic acid, a name which is still applied to it, because of its connection with the compound Prussian blue. Its chemical name, hydrogen cyanide or hydrocyanic acid, is derived from the word *cyanogen*, meaning blue or dark



blue, because the compound cyanogen was obtained from Prussian blue.

(b) CYANOGEN.

**Preparation.** — When a solution of potassium cyanide is treated with a soluble salt of mercury, like mercuric chloride ( $\text{HgCl}_2$ ), they react thus : —



Mercuric cyanide ( $\text{Hg}(\text{CN})_2$ ) is insoluble in water, and consequently can be separated out by filtration. When the dry salt is heated, it breaks up into free mercury and a gaseous compound called cyanogen.

**Properties of Cyanogen.** — Cyanogen is a gas having a density of 26, corresponding to the formula  $\text{C}_2\text{N}_2$ . If nitrogen has a valence of 3, the compound can be represented thus : —



that is, CN has an unsatisfied valence which may be satisfied by another group like itself or by hydrogen, potassium, etc.

The gas is very poisonous and has an odor resembling prussic acid. It is soluble in water, but soon decomposes, having among its products ammonia and hydrogen cyanide ( $\text{HCN}$ ). It is easily oxidized.

## A STUDY OF COMBUSTION AND FLAMES.

(I.) **Combustion, (a) Nature of.** — The term *combustion*, as used by Lavoisier, its originator, means the union of the oxygen of the air with other elements, the action being often accompanied by light and heat. Others have defined combustion as

an act of chemical union accompanied by the evolution of light and heat. According to the latter definition, the union of antimony with chlorine or bromine is an act of combustion, since it is chemical union accompanied by light and heat, but no oxygen enters into the change. The direct union of oxygen with the elements is always accompanied by heat, but light is not always produced. In science all terms must have a definite meaning. It is better therefore to restrict the term *combustion* to all cases of chemical action accompanied by the evolution of heat, and usually light, in which pure oxygen or the oxygen of the air takes part.

Most of the cases of combustion which are ordinarily observed are those in which oxygen and an organic compound or free carbon are the substances that react chemically. In all such combustions there is a large amount of heat and light given out, or, in other words, a large amount of energy is given out in the form of heat and light. From these chemical actions come a large part of the energy used in doing the manufacturing of the world. The energy of men and animals comes from the same source,—the oxidation of organic compounds. As has been pointed out, the source of this energy is found in the sunbeam or in the sun. The organic compounds used for fuel are compounds containing carbon and hydrogen; for example, petroleum, illuminating gas (largely), and oils—or compounds containing carbon, hydrogen, and oxygen; and in much less quantity compounds containing carbon, hydrogen, oxygen, and nitrogen. These latter forms of fuel are illustrated by the different varieties of bituminous coal, peat, and wood.

The term *combustibles* includes all substances that unite with oxygen readily, heat, and sometimes light, being produced. All other substances are non-combustibles. Wood, coal, and peat illustrate the combustibles, and water and carbon dioxide are examples of the non-combustibles.

The attempt to distinguish between a supporter and a non-supporter of combustion is of no scientific value. Two substances, at least, are required in every case of chemical action and in every case of combustion. No ordinary combustion can take place without oxygen, but the fuel which supplies the hydrogen and carbon is just as necessary to the combustion as is the oxygen.

Heat always accompanies combustion, but not always light. A hundred kilogrammes of wood may be oxidized rapidly, and the amount of light and heat given out can be measured. The same amount of wood may slowly decay, or oxidize, and finally form the same products as in the case of rapid oxidation, but no light is given out. The heat, however, is exactly the same in quantity whether the combustion is slow or rapid, providing the final products are the same. There is this difference, however: in the case of rapid combustion, the final products are the only ones formed, while in decay or slow combustion there may be many intermediate products formed. Notice the case of the rusting of iron on the one hand, and the rapid oxidation of the same in pure oxygen. In case of the rusting, there is no apparent production of heat or light, while in the latter case a large amount of heat and light are evolved.

**Explosives.** — One, often both, of the substances that take part in combustion is usually in the form of a gas. If both substances are gaseous, and they are mixed before combustion begins, the action is rapid, owing, in part, to the free movement of the molecules of the substances, and the consequent ease with which the action is transferred to every part of the mass. If there is great chemism between the gaseous substances, or between particular elements of the substances, then the action produces explosive effects, since the heat of the reaction expands the gaseous products, although there may be no increase in their volume under the same conditions due to the new products themselves.

It is readily seen that the character of such explosions depends on two factors at least; namely, upon the volume of the product and the degree of temperature produced by the chemical union. For example, when 2 vols. of nitric oxide (NO) are mixed with 1 vol. of oxygen, chemical action takes place and nitrogen dioxide is formed. The volume of the product is less than that of the mixed gases, and the heat of the reaction is so small that the temperature of the product is only slightly raised. Compare this result with that produced when hydrogen and oxygen unite to form water, as to the volume of the product and the heat evolved.

Again, explosive results often follow when the substances that enter into the change are all solids or all liquids. In both cases, however, the substances must be intimately mixed, and there must be the formation of a gaseous product or products, accompanied by the evolution of a large amount of heat. For example, gunpowder is an intimate mixture of potassium nitrate ( $\text{KNO}_3$ ), carbon, and sulphur. (See under POTASSIUM NITRATE.) When chemical action is produced, a large volume of gases is produced and much heat is evolved. In general, such mixtures require a rise of temperature in a part of the mass, at least, to start the action.

Finally, there are chemical compounds formed under certain conditions, that under the effect of a slight rise of temperature, or even by a concussion, explode, or combustion goes on rapidly without the action of a second distinct body. In such cases there is a rearrangement of the atoms of the molecule into more stable compounds. This means the development of a large amount of heat. When the system is once disturbed, the change goes on until equilibrium is produced. Such a system may be compared, in a general sense, to a steel spring held in its coiled condition by a delicately adjusted catch. When this catch is removed the spring returns to a state of stable equilibrium. Energy is consequently always given out as

the result of an explosion. Chemical combinations and work may be done as the result. Examples of such work are seen when rock masses are moved by the explosion of dynamite, guncotton, etc. In gas engines the energy given out in the explosions of the gases used is employed to run machinery, etc.

**(b) Products of Ordinary Combustion. — Experimental Study, No. 62.** — Ignite a candle and lower it into a bottle of dry air; cover the bottle and allow the whole to stand as long as the action continues. Notice what collects on the cool parts of the bottle. Test the contents of the bottle for carbon dioxide. Examine a piece of carbon in the same way.

A tallow candle consists largely of a compound having the formula  $C_3H_5(C_{18}H_{35}O_2)_3$ . In complete combustion it is readily seen that water and carbon dioxide are the products. If the compound contains nitrogen, what would become of it?

Wood, illuminating gas, and in general all substances used as fuel, are composed of these elements, carbon, hydrogen, and oxygen, and the principal products of combustion are in complete oxidation, carbon dioxide, and water.

**(c) Temperature of Ignition.** — Here we have only to recall the study of carbon disulphide, illuminating gas, and in fact the many cases of the union of the elements with oxygen to understand that every oxidizable substance has its own temperature of ignition, or the temperature at which rapid chemical action takes place. These temperatures vary greatly. Substances like iron require very high temperatures before rapid action begins. (See oxidation of iron under study of oxygen.) Iron requires a temperature of about  $1200^\circ$ ; ordinary coal gas, about  $900^\circ$ ; hydrogen,  $500^\circ$  to  $600^\circ$ ; phosphorus,  $50^\circ$ ; etc.

In general, gases ignite more easily and oxidize more rapidly than do solids or liquids. It is also true that the temperature must be kept up to that necessary for ignition, or action ceases.

An ordinary match is a good illustration of many of these facts. The essentials of a match are, we will say, phosphorus, sulphur, and wood. The phosphorus inflames at a temperature of about  $50^{\circ}$ , and this temperature is easily produced by friction. The sulphur ignites at  $250^{\circ}$ , a temperature produced by the oxidizing of the phosphorus. The wood requires a temperature of  $800^{\circ}$  to  $1000^{\circ}$ , the necessary heat for which is produced by the oxidizing of the sulphur.

**Experimental Study, No. 63.** — Place a piece of wire gauze (copper best) about 10 cm. square, about 3 cm. above the Bunsen burner. Turn on the gas and bring a match near the escaping gas and above the gauze. Vary the distance of the gauze from the top of the lamp. Use gauze of different sized meshes if at hand. Why does the gas burn on the top of the gauze and not below it? Are copper and iron good conductors of heat?

Davy's safety lamp is based on the fact illustrated in the experimental study just given. This is an oil lamp, the flame of which is surrounded by wire gauze. When the miner enters the mine where there is fire-damp mixed with the air, say, for example, in quantities sufficient to form an explosive mixture, he is warned of the fact by the burning of the mixture on the inside of the gauze protector. The flame does not pass outward until it has heated the wire to the temperature of ignition, thus giving the miner a timely warning.

(II.) **Flame.** — (A) **Character of.** — **Experimental Study, No. 64.** — (a) Place fine pine shavings or sawdust in a large test-tube prepared to make and collect gas over water. Heat the tube carefully, rejecting the first bottle of gas. Heat as long as any gas escapes, collecting a sufficient number of bottles of gas for its study.

(b) Ignite the jet of gas and put a cold body in the flame. Note the product. Explain source of the elements of this compound.

(c) Bring the burning jet into a gas bottle and hold it there

as long as the action continues. Test the contents of the bottle with lime-water.

(*d*) Allow the bottle of gas to stand for some time over water and then examine its physical properties.

(*e*) Examine the residue in the tube from (*a*). Ignite it. Does it oxidize, producing a flame?

(*f*) Treat powdered bituminous coal in the same manner as the wood shavings; that is, from (*a*) to (*e*), inclusive.

(*B*) **Parts of Flame.** — (*1*) **Candle Flame.** — **Experimental Study, No. 65.** — (*a*) Prepare a tube 25 to 30 cm. long with about two inches of one end bent at an angle of  $30^\circ$  with the horizontal position, and place the bent end just above the end of the wick of the burning candle. Notice the gas passing up the tube. Ignite it. Whence is this gas? Is the substance of the candle volatile? What is evidently being produced?

(*b*) Bring a cold body, like a porcelain plate or evaporating-dish, down horizontally on the flame about to the end of the wick and remove quickly. What is the deposit? What is its source?

(*c*) Place a match horizontally in the flame of the candle and just above the end of the wick and about the middle of the match. When it is ignited, remove and examine, and note the part of the match that has been charred. What does this show in reference to the temperature of the different parts of the flame?

(*2*) **The Bunsen Lamp Flame.** — (*a*) Examine this flame in the same manner as the candle flame has been examined. Study the Bunsen lamp and determine and explain the use of its parts.

(*C*) **Luminosity of Flame.** — **Experimental Study, No. 66.** — (*a*) Place a cold body in a pure Bunsen flame and remove quickly. Note the effect on the color of the flame.

(*b*) Shut off the air and place a cold body in the flame as before. Explain the difference in the result.

(c) Prepare a fine powder of carbon (charcoal) and allow it to fall from 20 to 30 cm. above the pure Bunsen flame. Use iron filings also in the same way. Explain the result.

(d) Mix four parts of potassium chlorate ( $\text{KClO}_3$ ) with one part of dry strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ). Fill the deflagrating-spoon nearly full of the mixture and fuse it, holding it in the tip of the Bunsen flame. When well fused, lower it into the interior of the flame. Note and explain the results and the conditions imposed. What is the general character of these substances? To what was the increase in size of the flame due?

(e) If possible to do it, pass a mixture of the air and the gas from the tap through a red-hot tube before burning it in the burner.

(f) Arrange the burner so that it gives a colorless flame, and then cool by ice or snow the tube through which the gas passes. Recall the hydrogen flame. Which is hotter, the hydrogen flame or the ordinary gas flame? Why is the Bunsen flame non-luminous?

Explain the Argand burner. What is the effect of shutting off the central draught? How should the air be regulated as to quantity for any luminous flame?

**Character of Flame.** — When a piece of wood (in fact, most organic matter) is heated sufficiently hot, gases escape, and there remains a residue of solid carbon. If now this carbon is ignited in the air, it oxidizes without producing any flame, while the gas produced by the destructive distillation of wood does produce a flame when oxidized.

A flame, therefore, is a mass of gas, or gases, undergoing oxidation. If the pressure of the gas is kept up to a constant quantity, the size of the flame, everything else being equal, depends on the rapidity with which the gas is supplied, if the oxidation takes place in the air. Ordinary illuminating gas is produced by the destructive distillation of bituminous coal.



The coal consists largely of carbon, oxygen, and hydrogen, and under the influence of heat the atoms rearrange themselves, producing gaseous, volatile, liquid, and solid products. The solid product is called coke, and is carbon and the inorganic substances or the ash of coal. The gaseous products of the distillation, which are used for illuminating purposes, consist on the average in 100 vols. of 48 vols. of hydrogen, 35 vols. of marsh gas, 9 vols. of carbon monoxide, 2 vols. of carbon dioxide, 5 vols. of gases rich in carbon, like olefiant gas ( $C_2H_4$ ), etc. The remaining volumes are made up of nitrogen and oxygen.

Ordinary fire, whether produced from wood or bituminous coal, is a process of destructive distillation, with the difference that the gases produced are oxidized as rapidly as they are made.

**Parts of the Flame.** — When the flame of a candle is examined, it is found to consist of three parts, or zones. Beginning with the interior, there is a zone of hot gas supplied from below, being the result of the decomposition of the substance of the candle, as has been already pointed out; next there is a light-giving zone; and finally, an outer zone faintly luminous, in which the oxidation is complete. Thus the flame of the candle is supplied from below with gas unmixed with free oxygen, its molecules moving outward and upward. These outgoing molecules are met by molecules of air moving towards the flame, particularly from its sides. (Why?) The latter thus push their way in among the outward-moving gas. When these molecules reach a point where the temperature is sufficiently high, they unite with the carbon and hydrogen, and the products are carried upwards out of the regions of oxidation. The limit of the zone where perfect oxidation takes place, therefore, will be determined, in large part at least, by the velocity of the outward-moving gas. Of course there are other elements in the problem of complete oxida-

tion which will modify the position of the outer zone of the flame ; for example, the temperature of the flame, which will depend on the chemical character of the gas supplied, conditions of the atmosphere, etc.

**Bunsen Flame.** — The Bunsen lamp when the openings below are shut is like a candle ; that is, there is a readily oxidizable gas constantly supplied from below, which is moving outward with a certain velocity depending on the pressure from the gasometer. When the openings allow the entrance of the air from below, it is drawn in by the current of gas, and the heat produced by the oxidizing of the gas above, so that the escaping gas is a mixture of air (oxygen) and the oxidizable gas. If sufficient air is admitted, the oxidation is complete. This more complete oxidation is said to be due, at least in part, to the dilution of the gas rather than to the extra supply of oxygen. This can be shown by adding to the gas supply such inactive gases as carbon dioxide, nitrogen, etc.

**Luminosity of Flame.** — The luminosity of the flame produced in ordinary cases of combustion is due principally to yellow (to white) hot particles of carbon. If a cold body is placed in such a flame, the particles are cooled down below red heat, and they adhere to the body in the form of soot. When an ordinary kerosene lamp wick is turned up "too high," more gas is set free than can be oxidized, and the carbon is carried upwards into regions which are heated below the temperature of ignition, as well as into regions which are nearly free from oxygen.

In general, the luminosity of a flame increases with an increase in the temperature of the gases producing it. This is only true of gases of the same kind. The density of the gas producing the flame also effects its luminosity. Thus the oxyhydrogen flame, which is much hotter than any ordinary gas flame, is non-luminous ; but if the gas is oxidized under a pressure of about 20 atmospheres, a luminous flame is produced.

The changing of a luminous flame to a non-luminous one may be said to be due to two causes.

(a) As has just been seen, it is due, in part, to the dilution of the gas, for example, with air.

(b) When such a flame is luminous, the carbon compounds of the gas must be broken up before the particles of carbon are set free. Now as a matter of fact it requires a higher temperature to decompose these gases when diluted than it does when they are undiluted. This can be shown by heating the mixture of air and gas by passing it through a red-hot tube before igniting it, when it becomes luminous again. The diluted gas burns with a colorless flame because this decomposition does not take place, but the carbon passes directly to carbon dioxide; but at the higher temperature it does become decomposed. Again, chlorine gas decomposes the carbon compounds occurring in ordinary gas at the temperature of the Bunsen flame, and when it is mixed with the gas, the flame becomes luminous again, due to the free carbon.

**Oxidizing and Reducing Flames. — Bunsen Flame.** — (a) In oxidizing any substance, heat is either necessary or aids in the rapidity of the action. As has been seen in the study of the Bunsen flame, its outer portions are supplied with oxygen from the air reaching it from the outside, and also from air mixed with the gas entering at the openings below. If now a substance that takes oxygen when heated be placed in the outer parts of the flame, it becomes oxidized, and this portion of the flame is called the oxidizing flame. Again, if the air be so shut off that the tip of the inner cone is luminous, there is found a portion of flame where the supply of oxygen is at a minimum, and any substance containing oxygen that is placed there loses its oxygen to the oxidizable gas, providing, of course, it yields its oxygen at the temperature produced. This portion of the flame is called the reducing flame.

(*b*) **Blow-pipe Flame.** — For purposes of concentration and direction of the flame a mouth blow-pipe, or a bellows blow-pipe, is commonly used. The student should study and describe the blow-pipe. (The blow-pipe worked by the bellows is preferable to the mouth blow-pipe.)

When the mouth blow-pipe is used, the tip of the pipe is placed in the centre of the inner cone of a Bunsen flame, when the air is shut off below and it is reduced to the proper size. The flame, by gentle pressure of air with the cheeks, is directed on the substance to be acted upon. The substance is held in the outer part of the flame as far as possible toward the tip, as was done in the case of the Bunsen flame, if it is to be oxidized, and in the inner cone if it is to be reduced. The best reducing flame is produced by placing the tip of the blow-pipe just inside the luminous flame of the Bunsen lamp, blowing over rather than through it. In this flame the oxidization is less perfect, and therefore contains matters to be oxidized, the oxygen being in part supplied by the substance to be reduced. The substance to be reduced is held so that the luminous cone covers it, and a blast sufficient only to direct a flame should be used.

These two flames should be studied and the production of each carefully made out. One method is to melt some oxidizable metal like lead or tin, and heat each in the flame, determining in which flame the film of oxide appears and in which one it disappears.

---

## OXIDES AND ACIDS OF SILICON.

**Occurrence and Distribution.** — The oxide of silicon, commonly known as silica, occurs in large quantities in nature and is widely distributed. It occurs, also, as a part of many animal

and vegetable organisms. It forms a part of the stems of many plants, like wheat and corn, serving to strengthen and stiffen them. It occurs in sponges, in the feathers of certain birds, and in the hard parts of minute plants, called diatoms. As quartz, silica forms one of the principal constituents of all granite. Quartz is known under a variety of names depending on crystalline form, transparency, color, etc.

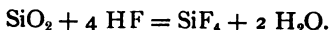
Rock crystal is nature's purest crystalline quartz or silica. Amethyst, rose quartz, and smoky quartz are examples of more or less impure forms of silica. The color of the varieties is due to the small amount of the oxides of metals present with the silicon oxide; for example, amethyst is colored by manganese oxide.

Another variety of natural silica is amorphous, or it may be a mixture of the amorphous form and the crystalline variety. Examples of such forms are opal, chalcedony, onyx, agate, flint, etc. These are transparent or translucent. Other varieties are opaque, such as jasper, sandstone, bloodstone, and the so-called silicified wood.

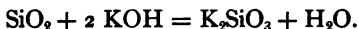
Silica also exists as sand, and in sandstone, forming large rock masses of great practical and geological interest. The sandstones are among the best building-stones, as for example, brown and red sandstone.

**Preparation.** — Only one oxide of silicon has been prepared. It can be prepared by the oxidation of silicon, or by oxidizing hydrogen silicide. It can also be produced from compounds called silicates, and silicic acid, and especially from the alkaline silicates.

**Properties of Silicon Dioxide.** — Silicon dioxide, at ordinary temperatures, resists the action of most of the chemical agents. It is insoluble in water, and in all acids except hydrogen fluoride. This acid decomposes it, producing water and silicon tetrafluoride.

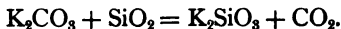


Crystalline silicon dioxide in the form of quartz is very hard, so hard that it scratches glass and is 7 in the scale of hardness of minerals. It is fused ~~only~~ at the temperature of the oxyhydrogen flame. The amorphous varieties are dissolved in solutions of the alkalis, or are decomposed by boiling in alkali carbonate solution forming compounds called silicates. The crystalline varieties are not thus dissolved.



Compare this reaction with the action of potassium hydroxide (KOH) on sulphur dioxide ( $\text{SO}_2$ ).

All varieties when fused with the alkali hydroxides or with the alkali carbonates produce the corresponding silicates.



Compare this reaction with the action of the other non-metallic oxides on the carbonates.

**Formula.** — The formula of the compound of silicon and oxygen cannot be determined by the vapor density method, since it is absolutely non-volatile at any temperature to which it has been submitted. Silicon, as we have seen, forms several volatile compounds with other elements; *e.g.* with hydrogen and chlorine, and in all cases it has a valence of 4. According to this fact its formula is given as  $\text{SiO}_2$ , agreeing with the results of quantitative analysis.

**Uses.** — Many of the forms of silicon dioxide found in nature are used in jewelry, and for ornamental and optical purposes. Such forms are amethyst, agate, rock crystal, cat's-eye (a variety of chalcedony), onyx, flint, etc. Sand is a necessary substance in making glass and mortar. (See under GLASS and PORCELAIN.) Sandstone furnishes the most desirable building-stone. Infusorial deposits are used in making dynamite.

## SILICIC ACID.

Theoretically, this acid is formed by dissolving the oxide in water. When, however, this oxide is once separated from water, it becomes insoluble and is not at all acted upon by it. When the alkaline silicates are decomposed by an acid, the hydrogen takes the place of the base, and the acid is thus formed.

**Experimental Study, No. 67.** — (*a*) Fuse in a platinum or porcelain crucible a mixture of 1 g. of pure sand and 3.5 g. of dry sodium carbonate, or a fusing mixture consisting of equal parts by weight of potassium and sodium carbonate. Heat until there is quiet fusion. Determine what the gas is that escapes.

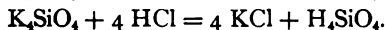
Before the mass has solidified pour it out on a smooth stone, and when cool powder it, and treat the powder with 30 cc. of water, boiling it until it is all dissolved. Filter if it is necessary to obtain a clear solution.

(*b*) Treat 5 cc. of the solution with hydrochloric acid, pouring the alkaline silicate into the dilute acid.

(*c*) To 5 cc. of the solution add 30 cc. of water, and treat with the same acid as in (*b*). Of what does the first solution consist? What effect on these substances will the acid have? Write the reaction when  $\text{H}_2\text{SiO}_3$  is formed.

(*d*) Treat the remainder of the solution with hydrochloric acid. Evaporate the solution to dryness, and boil the residue in water, and filter. Remove the residue from the filter, heat it to redness, and compare with common sand.

**Properties of Silicic Acid.** — When the mass produced by fusing natural silicon dioxide with sodium carbonate is treated with water and hydrogen chloride, the silicate produced by the fusion is decomposed, and hydrogen silicate is formed as a gelatinous mass.



If the solution of the silicate is dilute, most of the silicic acid or hydrogen silicate remains in solution, and may be separated by dialysis. (Dialysis depends on the physical fact that many substances in solution pass through porous membranes, while others do not pass through at all. Such membranes are represented by the bladder of animals and parchment paper. In general, substances that do not crystallize do not pass through the porous diaphragm, while crystalline substances do pass through.) If now the solution containing silicic acid and potassium chloride or sodium chloride, as the case may be, is placed in the dialyzer, the silicic acid remains in the inner vessel, while the potassium chloride and the hydrogen chloride pass into the pure water in the outer vessel. A solution containing about 5 per cent of silicon dioxide can be prepared in this manner. It may be concentrated further to a solution containing 14 per cent by evaporating over sulphuric acid.

The silicic acid probably has the formula  $\text{H}_4\text{SiO}_4$  or  $\text{Si}(\text{OH})_4$ . This compound is sometimes called normal silicic acid; that is, a compound in which all of the valences of the silicon are satisfied by hydroxyl. The acid that deposits on further evaporation of the 14 per cent solution has the formula  $\text{H}_2\text{SiO}_3$  or  $(\text{HO})_2\text{SiO}$ ; that is, the normal acid loses one molecule of water. The last acid is called metasilicic acid, corresponding to metaphosphoric acid. When the metasilicic acid is heated, several hydroxyl compounds may be formed by the loss of water, but finally silicon dioxide is left.

**Silicates.** — There are only a small number of salts corresponding to the normal silicic acid ( $\text{Si}(\text{OH})_4$ ) that are known, and these are mostly formed with rare metals like zircon and thorium, in the minerals zircon and thorite. They are represented by the formulæ  $\text{ZrSiO}_4$  and  $\text{ThSiO}_4$ , respectively. Magnesium silicate, crysolite, has the formula  $\text{Mg}_2\text{SiO}_4$ .

There are salts corresponding to normal silicic acid minus one molecule of water,  $\text{H}_4\text{SiO}_4 = \text{H}_2\text{SiO}_3 + \text{H}_2\text{O}$ . The salts



of this acid are called metasilicates, and are illustrated by such salts as potassium and sodium, metasilicate ( $K_2SiO_3$  and  $Na_2SiO_3$ ). Other acids are formed and also their corresponding salts by the removal of water from two or more molecules of these acids, *e.g.* :—



The salts of the acids are called disilicates. The trisilicate, or trisilicic acid, is formed from three molecules of the normal acid, and from this acid the trisilicates are formed. Thus :—



The number of the polysilicates found in nature is quite large. Enough, however, has been given to indicate their complexity, and further statements in regard to them are deferred until the bases forming these silicates are studied.

The silicates are all insoluble in water except those of potassium and sodium ; these alkali silicates are called soluble glass.

## BORON.

**Occurrence and Distribution.**—Boron does not occur free in nature, as its affinity for other elements and especially for oxygen is quite strong. It occurs chiefly as compound of hydrogen, oxygen, and boron, or boric acid, and as borax, a sodium salt of pyroboric acid. Its compounds are not widely distributed, but are found chiefly in the volcanic regions of California, Tuscany, and Thibet.

**Methods of Preparation.**—Amorphous boron is prepared from its oxide by fusing the latter with sodium or potassium.

A crystalline variety is produced by fusing the amorphous form with aluminium. Explain the action of the sodium or potassium.

**Preparation.** — Heat 10 g. of boric acid until it is anhydrous; cool, and powder it to a fine powder. Now place in the bottom of a hard glass tube a clean piece of sodium as large as a pea, and cover it well with the powdered anhydride. Heat the tube until the sodium disappears. (A slight detonation may occur.) When the tube is cool, break it, and remove the residue, and treat with dilute hydrochloric acid. The anhydride has the formula  $B_2O_3$ . What is the reaction with sodium? The insoluble residue is the boron.

**Experimental Study, No. 68.** — (a) Dry and heat a bit of the amorphous boron in the air. Does it oxidize? Did it oxidize at ordinary temperatures in the air?

(b) Heat another portion of the boron in pure nitrogen gas. The boron is heated to white heat in a tube through which nitrogen gas is passing. Of what must the compound consist?

(c) Fuse the remainder with aluminium, allow it to cool, and treat the residue with dilute hydrochloric acid. Examine the crystals remaining unchanged by the acid.

(d) Thoroughly mix boric oxide and powdered magnesium. Place in a hard glass tube and cover over with more oxide or with common salt. Heat to white heat and examine the product. Test a little of the mass with hydrochloric acid. Note what gases escape. Ignite the gas as it escapes.

**Properties of Boron.** — Boron can be prepared in at least two forms, — the amorphous and crystalline. The amorphous form is a brown powder without taste or odor. It is fused with great difficulty, requiring the highest temperatures. It is only slightly acted upon by water. The amorphous variety of boron readily unites with oxygen, forming boric oxide. It is oxidized by nitric acid, and decomposes steam at red heat, forming the oxide of boron and free hydrogen. It possesses

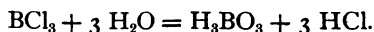
the peculiar property of uniting with nitrogen, forming the compound BN, or nitride of boron. It unites readily with the halogens.

The crystalline variety is very hard, so hard that it readily scratches glass and the ruby. It is not pure boron, however, but is an alloy of boron and aluminium, although it forms a large part of the alloy. The atomic mass of boron is 11.

### *Compounds of Boron.*

(a) **With Hydrogen.** — This compound has been recently prepared by heating finely powdered magnesium with boron anhydride ( $B_2O_3$ ). A portion of the magnesium unites with the boron, and a portion with the oxygen. When the mixture is treated with hydrochloric acid, hydrogen is set free mixed with a compound containing hydrogen and boron. This latter compound is probably boron hydride ( $H_3B$ ). (The valence of boron is determined to be 3 by a study of its volatile compounds.)

(b) **With Chlorine.** — When boron is heated in pure chlorine gas, the two elements unite, forming a colorless volatile liquid, which boils at  $17^\circ$ . The compound is also produced by heating boron oxide with carbon and pure chlorine gas. (What is the effect of the carbon? Why does not chlorine alone separate the boron from the oxygen?) The chloride is decomposed by water, forming hydrogen chloride and boric acid.



**Determination of the Formula of the Compound of Boron with Chlorine.** — The vapor density of the compound of boron with chlorine is 58.55, and consists of 9.4 per cent of boron and 90.6 per cent of chlorine.

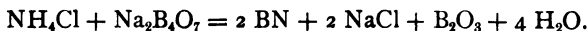
Four gaseous molecules containing boron have been studied, and in none of them is there a less amount of boron than in

this one. Determine the atomic mass and valence of boron and the formula for the chloride.

(c) **With Bromine.** — Bromine forms a compound with boron in the same manner in general as does chlorine. The compound is a liquid, boiling at  $90.5^{\circ}$ . Its vapor is colorless and has a density of 125.1. The percentage composition of the compound is 4.382 of boron and 95.618 for bromine. Determine its formula. In its behavior toward other substances it resembles chlorine.

(d) **With Fluorine.** — Fluorine unites with boron, forming a gaseous compound having the formula  $\text{BF}_3$ . When this compound is brought in contact with water, it is decomposed, and forms boric acid and a compound having a formula  $\text{HBF}_4$ . This latter compound has acid properties and forms salts with bases, and especially with the alkaline bases. The acid is called fluoboric acid, and the salts fluoborates.

(e) **With Nitrogen.** — The compound of boron with nitrogen is produced by heating it to a white heat in a tube through which nitrogen or ammonia is passing. Boron nitride is also prepared by heating ammonium chloride with absolutely anhydrous borax.



This compound is of interest, since it presents the peculiarity that it is a stable compound of nitrogen with another element than hydrogen. It is a solid, existing as a white powder, insoluble in water, and in general is a very stable compound. Its stability is shown by the fact that steam requires to be heated to red heat before it decomposes the nitride.

(f) **With Oxygen.** — Boron unites with oxygen in but one proportion, which according to the valence just determined is represented by the formula  $\text{B}_2\text{O}_3$ . This compound is a brittle solid, and when fused resembles glass in general appearance. It is obtained from boric acid by heating it to expel the water,

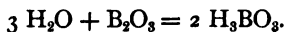
or it is prepared from the amorphous boron by heating the latter in the air or in pure oxygen.

Boron oxide is not volatile except at the highest temperature. Analysis shows that it contains 68.57 per cent of oxygen and 31.43 per cent of boron.

In 100 parts of the oxide, the atomic masses of the elements being considered as known, there are 4.285+ atoms of oxygen and 2.857+ atoms of boron. These results represent the proportion of atoms. But since only whole atoms can enter into the molecule, whole numbers are sought that shall preserve this proportion. Taking 2.857 as the unit, or dividing both numbers by 2.857, the proportions become 1 to 1.5, or in whole numbers, 2 to 3; therefore the simplest formula the oxide can have is  $B_2O_3$ . Of course the formula can be any number of times this proportion; but when considered in connection with the fact that the valence of boron is 3, the formula for the oxide is fixed at  $B_2O_3$ . This method of determining formulæ is often applied to non-volatile bodies.

#### BORIC ACID.

**Occurrence and Distribution.**—This acid is formed when boric oxide is dissolved, or acted upon chemically, by water.



The acid also exists ready formed in nature in certain volcanic regions, and especially in Tuscany. As shown in the experimental study, the acid is carried along from its solutions by escaping steam. In Tuscany steam and gases escape constantly from openings in the ground, bringing up with them more or less of solid material. Basins are thus built up around these openings and become partly filled with water. The gases bubble up through this water, are condensed, and in time the

water becomes a weak solution of boric acid. These solutions are gathered and slowly concentrated by spontaneous evaporation, the necessary heat being supplied by the heat of the hot gases that escape. Thousands of tons of boric acid are thus made annually.

**Experimental Study, No. 69.** — (a) Dissolve in a porcelain evaporating-dish a gramme or less of boric acid in 20 cc. of alcohol. Ignite the alcohol, stirring the solution as it oxidizes. Note the color of the flame. This is a characteristic test for the acid and for boron.

(b) Dissolve 2 g. of boric acid in water. Test the solution for acidity. Boil the solution and bring the Bunsen flame into the escaping steam. Note the color of the flame. What does the result indicate?

(c) Fuse several crystals of the acid in the deflagrating-spoon, and while they are fused, touch the mass with a glass rod, pulling it slowly away.

(d) Treat a little borax in an evaporating-dish with alcohol; stir and ignite the latter. What effect does the borax have on the color of the flame?

(e) Treat a little borax in an evaporating-dish with sulphuric acid, stirring thoroughly. Add alcohol, stirring the mass, and then ignite the alcohol. Compare the result with (a).

(f) Make a saturated solution of borax, and add to it sulphuric or hydrochloric acid. Allow it to stand for ten minutes, and decant the liquid, and wash the crystals with a little water. To a little of the solid residue add alcohol and ignite. What has been set free? Borax being a sodium salt of pyroboric acid ( $H_2B_4O_7$ ), what action will sulphuric acid have on it? Is boric acid a weak or a strong acid?

**Properties.** — Boric acid ( $H_3BO_3$  or  $B(HO)_3$ ) is a solid crystalline substance. It is not very soluble in water at ordinary temperatures, 1 g. of the acid being dissolved in about 25 cc. of water. It is quite soluble in alcohol and in boiling

hot water. It is volatile with steam, sufficient being carried along with it to color green the flame of a Bunsen lamp held in it.

It is acid to litmus paper, and decomposes the alkaline carbonate at a boiling temperature. When its alcohol solution is oxidized, the flame is colored green, a characteristic test for the acid. Its salts are decomposed by most other acids, and especially by sulphuric acid, the boric acid being set free. It may be tested for by the alcohol flame test.

When the normal acid  $\text{H}_3\text{BO}_3$  is heated to  $100^\circ$ , it loses a molecule of water and forms metaboric acid.



If the heat is continued for some time at  $160^\circ$ , it loses still more water, and pyroboric acid or tetraboric acid is formed.



or



If the tetraboric acid is heated to higher temperatures, it loses another molecule of water and becomes two molecules of trioxide of boron.

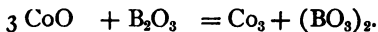
These acids of boron all form salts, but the tetraborates and the metaborates are the most stable. The normal borates are formed at fusing temperature and in the absence of water. In presence of water they are decomposed into the boric acid and salts of one or the other of the boron acids.

**Experimental Study, No. 70. — Bead Tests.** — Make a loop in the end of a platinum wire by winding it once around the sharpened lead of a lead-pencil. Heat the wire red-hot and dip it either in powdered boric acid or in borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$ ). Heat the mass until fused to a clear glass. The bead should be as large as a No. 6 shot. (Why does the borax bead swell up when first heated?) Dip the bead in a solution of cobalt

nitrate ( $\text{Co}(\text{NO}_3)_2$ ) and fuse it again. The color of the bead is characteristic for cobalt.

(*b*) Make other beads, using the hydroxides or oxides of nickel or manganese, and of copper. Heat the beads in the oxidizing flame; follow this by heating in the reducing flame. These results are characteristic for the substances mentioned.

Boric oxide and borax decompose salts whose acids are volatile at high temperatures, the bases uniting with the boric oxides to form normal borates and sometimes double salts. For example, heat decomposes cobalt nitrate, leaving cobalt oxide ( $\text{CoO}$ ). This oxide is dissolved and cobalt borate is formed, a substance having a characteristic blue color.



**Uses.** — Boric acid and its salts serve many useful purposes. For example, in soldering, the borax serves to dissolve away the oxide formed on the surface of the tin or iron, and thus a chemically clean surface is presented to the solder. It is used in glass-making (flint glass), and in enamelling or glazing porcelain; in the separation of metals from their ores, or as a flux (*fluo*, to flow); in making artificial gems; in candle-wicks, for stiffening felt hats, and as a preservative for various kinds of food, etc. Boric acid is a powerful antiseptic.

---

## GENERAL OBSERVATIONS AND RECAPITULATIONS.

**Classification of the Compounds Studied.** — The compounds studied thus far, on the basis of composition, may be arranged or grouped as hydrides, oxides, halides, and hydroxides; the latter term including bases and acids. These groups are: —



*Hydrides.*

HF or (H <sub>2</sub> F <sub>2</sub> )	H <sub>2</sub> O <sub>2</sub>	H <sub>3</sub> N	H <sub>4</sub> C
HCl	H <sub>2</sub> O	H <sub>3</sub> P	H <sub>4</sub> Si
HBr	H <sub>2</sub> S	H <sub>3</sub> As	
HI	H <sub>2</sub> S <sub>2</sub>	H <sub>3</sub> Sb	
	H <sub>2</sub> Se	H <sub>3</sub> B(?)	
	H <sub>2</sub> Te		

*Oxides.*

H <sub>2</sub> O	CO	P <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	I <sub>2</sub> O <sub>7</sub> (?)
P <sub>2</sub> O(?)		Cl <sub>2</sub> O <sub>3</sub> (?)	SO <sub>2</sub>	I <sub>2</sub> O <sub>5</sub>	S <sub>2</sub> O <sub>7</sub>
Br <sub>2</sub> O(?)		Br <sub>2</sub> O <sub>3</sub> (?)	SiO <sub>2</sub>	Cl <sub>2</sub> O <sub>5</sub> (?)	Cl <sub>2</sub> O <sub>7</sub> (?)
I <sub>2</sub> O(?)		I <sub>2</sub> O <sub>3</sub>	SeO <sub>2</sub>	Br <sub>2</sub> O <sub>5</sub> (?)	Br <sub>2</sub> O <sub>7</sub> (?)
Cl <sub>2</sub> O		As <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	As <sub>2</sub> O <sub>5</sub>	
		B <sub>2</sub> O <sub>3</sub>	ClO <sub>2</sub>	Sb <sub>2</sub> O <sub>5</sub>	
		Sb <sub>2</sub> O <sub>3</sub>	Cl <sub>2</sub> O <sub>4</sub>		
		S <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>4</sub>		

*Halides.*

HF or (H <sub>2</sub> F <sub>2</sub> )	S <sub>2</sub> Cl <sub>2</sub>	PCl <sub>3</sub>	SCl <sub>4</sub>	PCl <sub>5</sub>
HCl	SCl <sub>2</sub>	PBr <sub>3</sub>	PI <sub>2</sub>	AsCl <sub>5</sub>
HBr		PI <sub>3</sub>	P <sub>2</sub> I <sub>4</sub>	SbCl <sub>5</sub>
HI		PF <sub>3</sub>	SiCl <sub>4</sub>	AsI <sub>5</sub>
		AsCl <sub>3</sub>	SiF <sub>4</sub>	PI <sub>5</sub>
		SbCl <sub>3</sub>	ClCl <sub>4</sub>	
		BCl <sub>3</sub>		
		(AsI <sub>3</sub> )(?)		
		BF <sub>3</sub>		
		AsF <sub>3</sub>		

*Hydroxides.*

H—O—H	SiO—(OH) <sub>2</sub>	PO—(OH) <sub>3</sub>	Si—(OH) <sub>4</sub>
Cl—OH	SO <sub>2</sub> —(OH) <sub>2</sub>	B—(OH) <sub>3</sub>	P <sub>2</sub> O <sub>3</sub> —(OH) <sub>4</sub>
Br—OH	SO—(OH) <sub>2</sub>		
I—OH(?)	SeO <sub>2</sub> —(OH) <sub>2</sub>		Te(OH) <sub>6</sub>
ClO—OH	TeO—(OH) <sub>2</sub>		S—(OH) <sub>6</sub>
ClO <sub>2</sub> —OH	HPO—(OH) <sub>2</sub>		
BrO <sub>2</sub> —OH	CO—(OH) <sub>2</sub>		
IO <sub>2</sub> —OH	B <sub>4</sub> O <sub>5</sub> (OH) <sub>2</sub>		
IO <sub>3</sub> —OH			
(N—OH)(?)			
NO—OH			
NO <sub>2</sub> —OH			
H <sub>2</sub> PO—OH			
SOH—OH(?)			
K—OH			
Na—OH			
NH <sub>4</sub> —OH			
PO <sub>2</sub> —OH			
ClO <sub>3</sub> —OH			
BO—(OH)(?)			

## HYDRIDES.

The hydrides are all gases, and nearly all of them are quite stable compounds at ordinary temperatures. They constitute all the binary compounds of hydrogen if a few unstable compounds with the metals are excepted. Such compounds as copper hydride (Cu<sub>2</sub>H<sub>2</sub>), potassium, and sodium hydrides (K<sub>2</sub>H and Na<sub>2</sub>H) are decomposed as soon as the peculiar conditions

under which they are formed are removed. Carbon forms a large number of compounds with hydrogen, the consideration of which constitutes a large part of Organic Chemistry.

All of these hydrides, except those of silicon, carbon, nitrogen, phosphorus, arsenic, antimony, and tellurium, are absorbed by water and produce solutions that are acid in character. The nitrogen compound when absorbed by water forms a solution that is alkaline or basic in character. The hydride of phosphorus possesses the same property as does that of nitrogen, although to a less degree. All of the hydrides, excepting those of the halogens, are readily decomposed by oxygen when heated with it, nitrogen hydride being the least readily decomposed. The compounds formed in this decomposition are water and the oxide of the element combined with the hydrogen.

When these hydrides are subjected to the action of a current of electricity, they are decomposed into their elements, the hydrogen always collecting at the negative pole, and the other element at the positive pole. The elements that form compounds with hydrogen are, therefore, electro-negative in respect to it. Thus the hydrogen in these hydrides acts as a body positively electrified does towards a negatively electrified body; *i.e.* it moves towards the negative pole of the current—the negatively electrified body.

Whether an element is electro-positive or electro-negative appears to be in some manner a function of the two or more elements that may combine. For example, chlorine and oxygen are both negative towards hydrogen, but when a compound of chlorine and oxygen are brought under the influence of an electric current, the chlorine is carried to the negative pole or it appears to be positive under these conditions.

Sulphur is positive towards oxygen, although negative towards hydrogen. The separation of the hydrides, the halides, the oxides, and the hydroxides, by electrolysis, shows, in each case, the elements themselves or some characteristic group of ele-

ments arranged at the two poles of the current in equivalent proportions ; and if the two parts are removed, either directly or by some secondary reaction, the action continues until the whole of the compound is decomposed.

The heat of formation is indirectly a measure of the chemism of hydrogen for the elements that with it form the hydrides. The heat of formation—or the amount of heat given up or absorbed during the formation of a mass of a compound represented by its formula from the masses of the constituents of the compound represented by the formulæ of these constituents—varies from 68,400 calories, for water, to — 37,100 calories, for hydrogen arsenide ( $\text{AsH}_3$ ). This is only a relative measure of the chemism of these elements, since the molecules must be separated into their atoms before the new combination can take place. This requires a portion of the heat energy produced in the change. Elements in the nascent state are more active than molecules of the same elements. This difference is accounted for when we consider that an element in this condition is atomic, or at least is in a simpler form than when it is in its ordinary molecular condition.

Again, allotropic forms of elements give out different amounts of heat when they combine with the same amount of the same element. For example, when 62 g. of yellow phosphorus is changed to the red variety, 43,100 calories of heat are evolved. When this same amount of yellow phosphorus is combined with oxygen to form the pentoxide  $\text{P}_2\text{O}_5$ , 369,900 calories of heat are evolved ; but 62 g. of red phosphorus evolve only 326,800 calories under the same conditions. This difference of 43,100 calories is the same as that evolved when the yellow is changed to the amorphous phosphorus. The thermal value of this latter change is expressed by the number 43,100.

The value of this and similar measurement lies in the fact that it gives the relative chemism of the elements that form compounds and aids in a general way in determining whether

a certain chemical action will occur. It explains, for example, such changes as are produced when a binary compound of hydrogen (or a metal) and bromine or iodine is treated with free chlorine. Consider, for example, the hydrogen compounds of these two elements. When chlorine unites with hydrogen, 22,000 calories of heat are evolved; for the corresponding compounds with bromine and iodine +8400 and -6040 calories, respectively, represent the amounts of the heat of formation. It can be readily inferred from these facts that chlorine will set these elements free from these compounds. We know that such are the facts and that iodine is freed before the bromine if the two compounds are acted on in the presence of each other. In this case if heat is used, the iodine enters into a new combination and is wholly set free from its original combination.

Seventy-eight parts of potassium combine with 16 parts of oxygen to form potassium oxide ( $K_2O$ ), evolving 97,200 calories of heat; 46 parts of sodium unite with 16 parts of oxygen to form sodium oxide ( $Na_2O$ ), producing 100,200 calories of heat. Potassium is the strongest base, since its oxide, when dissolved in water, evolves 12,400 more heat units than does the oxide of sodium under the same conditions. Consequently, the decomposition of this compound will require more heat energy than will sodium hydroxide.

Again, we should not regard these numbers, and many others of similar import that have been determined for other elements, as absolutely measuring the chemism of the atoms for each in any given compound, since the products of this change may exist in different physical or mechanical conditions from that of the elements or compounds that enter into the chemical change. Energy in the form of heat will be evolved or absorbed in producing these changes. For example, the oxygen that combined with the potassium to form potassium oxide was a gas occupying a relatively large volume to what

it does in the solid oxide. The condensation of the oxygen means the giving up of energy. There are many other facts that go to show that the heat of formation of compounds cannot be regarded as the absolute measurement of chemism, the discussion of which does not belong to an elementary work like this one. However, if the compounds of the various elements with chlorine or oxygen, for example, be arranged according to their heats of formation, the relative affinities of these elements for the particular element is readily shown.

### THE HALIDES.

The halides of the non-metallic elements are not very stable compounds, if the compounds of hydrogen with chlorine and fluorine are excepted. They are all easily decomposed by heat, are decomposed by water, forming, usually, the hydrogen halide and an oxygen compound of the other element. The chlorine compounds are best known.

In general, the non-metallic elements exhibit the same variability of valence towards the halogens that they do towards oxygen, and when these compounds are decomposed by water, the compound (usually acids) formed with the other element holds it with the valence unchanged. For example, phosphorus pentachloride ( $\text{PCl}_5$ ) reacts with water, forming phosphoric acid ( $\text{H}_3\text{P}^{\text{v}}\text{O}_4$ ).

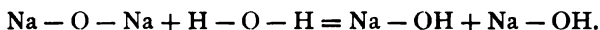
The halide compound containing the non-metallic element with its highest valence is usually formed from the lower compound by heating in excess of the halogen.

### OXIDES AND HYDROXIDES.

Oxygen has great chemism for all the non-metallic elements, except nitrogen and the halogens, and with most of them it forms two or more compounds. These oxides, when brought

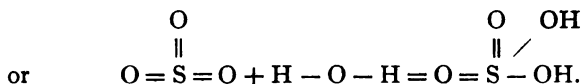
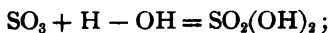
in contact with water, react with it, producing compounds, some of which are acids and some of which are alkalis or bases. Of those studied thus far, only two are basic in character,—those of potassium and sodium. These reactions consist in the union of the atoms of the two molecules to form a single molecule. The water and the oxide molecules are perfectly saturated molecules, since the oxygen unites with no more of the other elements under the conditions which produced them. The action is also purely a chemical one, since definite proportions enter into the action. It must be, therefore, that there is a rearrangement of the atoms in the molecules in order that these compounds can be formed. In the study of sodium and potassium it was shown that when these elements act on water one-half of the hydrogen is set free, and the new molecules have the formulæ  $K-OH$  and  $Na-OH$ ; *i.e.* potassium (or sodium) has taken the place of one atom of hydrogen in the molecule of water. If this new molecule ( $Na-OH$ ) is properly treated with more of the basic element, the other atom of hydrogen is replaced by an atom of sodium (or potassium), and a new molecule containing hydrogen is formed.

Now if sodium oxide (or potassium) is brought in contact with water, the following reaction occurs:—



The heat of formation of sodium hydroxide is about 6000 calories greater than that of sodium oxide. Hence, under these conditions, the hydroxide compound will be formed, and it may be said that the latter compound is more stable than is sodium oxide.

The acid oxide acts in a manner similar to that of the basic oxides. The action of water on sulphur trioxide may be represented thus:—



Here the sulphur of the trioxide has six units of valence, all of which are satisfied by the three atoms of oxygen. When the oxide is brought in contact with water, one molecule of water becomes two molecules of hydroxyl, taking the atom of oxygen necessary to form them from the trioxide. The corresponding units of valence of the oxide are satisfied by the two unsatisfied molecules of the hydroxyl group. The complete proof that the acids have the constitution given them in the table on a previous page perhaps has not been wholly made, but these acids act in many chemical changes as though this were their constitution, and this assumption explains these reactions. It may not be possible to know exactly the manner in which the atoms of any given molecule are grouped in its ordinary state of existence, but we do know how these molecules divide up in chemical actions, and that under the same conditions the actions always proceed in one way. Graphic illustrations of the constitution of molecules are attempts to picture the facts discovered at the time of chemical change. If it is asserted that a given compound contains hydroxyl, it practically means that under certain conditions hydroxyl always comes out of or goes into that compound.

Examine the products of the reactions of any one of these acids (for example, nitric acid) on a base like potassium hydroxide.



It is known that water and a compound having 39 parts of potassium, 14 parts of nitrogen, and 48 parts of oxygen is formed. In all similar reactions water is one of the products,

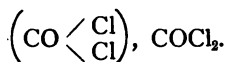


and the other compound in each case has exchanged hydrogen for the metal of the base. In cases in which all of the hydrogen of the acid cannot be removed as hydroxyl, the remaining hydrogen cannot be replaced by metals. This representation of the structure of these compounds represents facts only.

Not all of the oxides included in the table given on page 342 have been formed and studied, but acids corresponding to most of them are known. The oxides included in parentheses are those that have as yet only a theoretical existence.

In general, with the same element, the more oxygen that it has combined with it, the more strongly marked are its acid properties and the more stable is the compound. For example, hypochlorous acid ( $\text{HClO}$ ) is decomposed at low temperatures, while perchloric acid ( $\text{HClO}_4$ ) is sufficiently stable to be distilled at temperatures up to  $135^\circ$ . The salts of these acids relatively have the same stability. When potassium chlorate ( $\text{KClO}_3$ ) is heated to fusion, oxygen is given off, and there remains a compound having the formula  $\text{KClO}_4$ , potassium perchlorate, which does not decompose unless heated to higher temperatures.

Many of these oxides show that they are unsaturated compounds by the readiness with which they take up more oxygen or other elements under the proper conditions. In carbon monoxide the carbon appears to have a valence of 2, while in its hydrogen compound it has four units of valence. But this oxide unites readily with oxygen to form carbon dioxide ( $\text{CO}_2$ ), or with chlorine to form carbonyl chloride

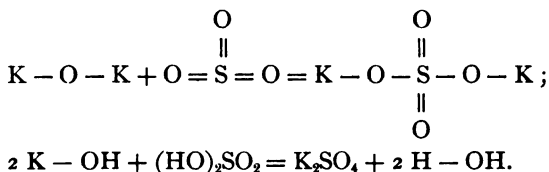


The remaining two units of valence are thus satisfied.

The amount of heat given out when these oxides are brought in contact with water varies from a few calories to a large number, showing, however, that the change is a chemical one.

The basic oxides ( $K_2O$  and  $Na_2O$ ) combine directly with the acid oxides and form salts identical with those formed by the action of the basic hydroxide on the acid hydroxide. In the first case there is but one substance formed, the salt; when in the second case, the salt and water are the products.

The reactions are —



**Valence.** — A study of the compounds given on pages 341–343 shows that the number of atoms of a given kind that another atom can hold in combination varies in many cases; that the number of atoms of hydrogen held by any of these atoms does not vary; that when the atom-holding power does vary, it varies with narrow limits, and that, in general, the common difference is two units. Again, considering the valence of elements as determined, the composition of molecules formed from them becomes known. The reader must bear in mind that the valence of the elements has been determined by a study of many of their compounds.

It is convenient to consider an acid as made up of two parts; namely, of the hydrogen that can be replaced by a metal, and the remainder of the molecule constituting a group of atoms that is always found in the salts of this acid. This may be called the salt or the acid radicle. Sulphuric acid, for example, has two atoms of hydrogen, all of which can be replaced by a metal, like potassium, and a group of atoms ( $\text{SO}_4$ ) that forms a part of all sulphates, and has a valence of 2. Consequently, the formula of any salt of this acid can be written if the valence of the metal that replaces the hydro-

gen is known. A metal "R" with a valence of 3 will form a salt having the formula  $R^{III}_2(SO_4)^n_3$ , since the units of valence of the elements or of any group of elements in any compound must be satisfied. Hypophosphorous acid has but one atom of replaceable hydrogen, and consequently the formula for its salt with the metal "R" is  $R(H_2PO_2)_3$ .

**Formulae.** — The molecular formulae of the hydrides, and of all the gaseous compounds, have been determined by the application of Avogadro's law, in connection with the facts of quantitative analysis, and the facts in reference to the changes and transformations of these substances. When the molecular mass is known, the relative atomic mass of the elements is readily established by bringing together the numbers that express the molecular masses; and since the percentage composition is known, the relative amounts of each element in the compounds can be determined. For any given element the smallest mass found in any molecule is the atomic mass of that element.

The formulae of the non-volatile acid, the atomic masses of whose elements are known, are determined by finding the number of atoms of hydrogen in the molecule according to the studies previously given, and thus the atoms of the other elements.

There are several other methods of determining the formulae of molecules of substances that are solids or liquids that cannot be converted in gases without decomposition. These will be brought forward later on. When the results of all these methods are found to agree in any particular case, it establishes more firmly the accuracy and correctness of these methods for other results in general.

# INDEX.

Acetylene, 184.  
 Acid, an, 101.  
     arsenic, 279.  
         tests for, 279.  
     arsenious, 277.  
         tests for, 278.  
     boric, 338.  
         tests for, 339.  
     bromic, 291.  
     carbonic, 300.  
     chloric, 288.  
     chlorous, 287.  
         formula for, 285.  
     hypobromous, 291.  
     hydrobromous, 48.  
     hydrochloric, 47.  
         tests for, 47.  
     hydrodic, 49.  
     hypochlorous, 283.  
         formula of, 285.  
     hyponitrous, 243.  
     hypophosphorous, 267.  
         tests for, 270.  
     hyposulphurous, 228.  
     iodic, 292.  
     metaboric, 340.  
     metaphosphoric, 267.  
     nitric, 244.  
         action on metals, 249.  
         formula of, 251.  
         natural formation of, 245.  
         reaction, 253.  
         tests for, 255.  
     nitrosyl sulphuric, 220.  
     nitrous, 253.  
         tests for, 255.  
     sulphuric, Nordhausen, 227.

Acid, sulphuric, normal, 223.  
     ortho-phosphoric, 263.  
     perchloric, 290.  
     periodic, 292.  
     phosphoric, 263.  
         formula for, 264.  
     phosphoric, glacial, 267.  
         tests for, 265.  
     phosphorous, 261.  
     pyroarsenic, 279.  
     pyrophosphoric, 267.  
     pyrosulphuric, 227.  
     selenic, 232.  
     selenious, 232.  
     silicic, 332.  
         normal, 333.  
     sulphocarbonic, 315.  
     sulphuric, 218.  
         manufacture of, 220.  
         action on salts, 224.  
         action on metals, 224.  
         tests for, 225.  
         formula of, 226.  
     sulphurous, 217.  
         formula of, 217.  
     telluric, 232.  
     tellurious, 232.  
     tetrahydroxyl sulphuric, 223.  
     thiosulphuric, 229.  
         tests for, 231.  
 Acids, relation to bases, 97.  
     of sulphur, higher, 231.  
     of sulphur, 213.  
 Agate, 330.  
 Air, 143.  
     composition of, 144.  
 Alkali, 97.

- Allotropism, 90.  
 Ammonia, 131.  
   reactions of, 140.  
   quantitative composition of, 136.  
   formula of, 139.  
   tests for, 141.  
 Ammonium, 140.  
   hydroxide, 140.  
 Analysis, 52.  
 Anhydride, sulphurous, 277.  
 Antimony, 167.  
   and the halogens, 173.  
   atomic mass of, 173.  
   tests for, 172.  
 Aqua fortis, 253.  
   regia, 257.  
 Arsenic, 159.  
   and the halogens, 166.  
   tests for, 165.  
   disulphide, 280.  
   pentasulphide, 280.  
   trisulphide, 280.  
   valence of, 276.  
 Atoms, 200.  
   define, 62-66.  
   mass of, 62.  
 Avogadro's law, 64.  
  
 Bases, 97-100.  
 Bleaching by chlorine, 35, 285.  
   by sulphur dioxide, 208.  
 Blow-pipe, oxy-hydrogen, 72.  
 Borax, 340.  
 Boron, 334.  
   bromide, 337.  
   chloride, 336.  
   fluoride, 337.  
   nitride, 336.  
   oxide, 337.  
 Bromine, 36.  
   tests for, 39.  
   atomic mass of, 56.  
  
 Carbon, 174.  
   allotropic forms, 183.  
   and silicon, 198.  
   atomic mass of, 190.  
   dioxide, 294.  
   Carbon, dioxide, and life, 301.  
     formula of, 297.  
     tests for, 301.  
   disulphide, 312.  
     formula of, 314.  
   reducing action of, 181.  
   monoxide, 305.  
     formula of, 309.  
     poisonous effects of, 311.  
   varieties of, 175.  
 Carbonates, 300.  
 Carbonyl chloride, 310.  
   sulphide, 316.  
 Chalcedony, 330.  
 Charcoal, 179.  
   properties of, 180.  
   animal, 182.  
 Chemical action, 14-61.  
 Chemistry, field of, 20.  
   methods of study, 23.  
 Chlorine, 32.  
   bleaching, 35, 285.  
   tests for, 36.  
   dioxide, 286.  
   hydrate, 35.  
   monoxide, 281.  
     formula for, 281.  
   pentoxide, 287.  
   trioxide, 286.  
 Choke-damp, 301.  
 Chlorates, 288.  
 Coke, 182.  
 Combustion, 318.  
 Combustibles, 319.  
 Cryolite, 42.  
 Cyanogen, 318.  
 Cyanides, 317.  
  
 Decay, 320.  
 Dialysis, 333.  
 Diamond, 177.  
 Diffusion, 26.  
 Disulphur trioxide, 228.  
   heptoxide, 228.  
 Dissociation, 76, 240.  
 Dynamite, 322.  
  
 Electrolysis, 80.

- Elements, 19, 344.  
   acid-forming, 103, 215.  
   base-forming, 103, 215.  
 Energy, 10.  
   conservation of, 22.  
   forms of, 11.  
 Equations, chemical, 104.  
   classification of, 106.  
 Experiment, 11.  
 Explosives, 320.  
  
 Fertilizers, 147.  
 Flame, 323.  
   Bunsen lamp, 324.  
   blow-pipe, 329.  
   luminosity of, 327.  
   oxidizing and reducing, 328.  
   parts of, 324.  
 Fluorine, 42.  
 Formulæ, 67, 352.  
   structure of, 204.  
  
 Graphite, 178.  
 Guano, 267.  
 Gunpowder, 250, 321.  
  
 Halides, 347.  
 Halogens, valence of, 293.  
   relations among, 43.  
   acids, quantitative composition of, 52.  
 Heat of formation, 127, 310, 345.  
   and chemism, 128, 179.  
 Hydrate, 223.  
 Hydrides, 343.  
 Hydrogen, 25.  
   antimonide, 170.  
     formula for, 173.  
   arsenide, 163.  
     formula for, 165.  
   boride, 336.  
   bromide, 48.  
   carbide, 184.  
     formula for, 188.  
   chloride, 44, 66.  
   cyanide, 316.  
   diffusion of, 26.  
   dioxide, 107, 110.  
   Hydrogen, iodide, 49.  
     fluoride, 50.  
     nitride, 131.  
     and platinum, 28.  
     phosphide, 153.  
       formula for, 156.  
     sulphide, 116.  
       formula for, 119.  
       tests for, 121.  
       reactions, 122.  
   selenide, 124.  
   silicide, 194.  
     formula for, 196.  
   telluride, 125.  
     tests for, 31.  
   Hydroxyl, 104.  
   Hydroxides, 103, 347.  
   Hypothesis, atomic, 61.  
     scientific, 60.  
  
 Ignition, temperature of, 322.  
 Indian fire, 280.  
 Iodine pentoxide, 292.  
 Iodine, 39.  
   tests for, 42.  
  
 Lamp-black, 182.  
 Law of causality, 23.  
   of constant proportions, 58.  
   Graham's, 30.  
   meaning of, 57.  
   of multiple proportions, 59.  
   of reciprocal proportions, 59.  
  
 Mass, 62.  
   atomic, 64, 199.  
   molecular, 64, 200.  
 Matches, 323.  
 Matter, 10.  
   classification of, 10.  
   forms of, 17.  
   conservation of, 21, 198.  
   constitution of, 61, 199.  
 Methane, 184.  
   and chlorine, 190.  
   properties of, 187.  
   quantitative composition of, 183.  
   reactions of, 197.

- Molecules, 63, 103, 199.  
     binary, 101.  
     elementary, 68.  
     size and number, 202.  
     ternary, 101.
- Nascent state, 90, 110.
- Neutralization, 99.
- Nitrates, 244.
- Nitric oxide, 236.  
     formula for, 239.
- Nitro-hydrochloric acid, 257.
- Nitrogen, 129.  
     dioxide, 239.  
     and explosives, 129, 250.  
     monoxide, 232.  
         formula of, 235.  
         reactions of, 236.  
     oxides and water, 243.  
     pentoxide, 240.  
     trichloride, 142.  
     trioxide, 240.  
     tests for, 131.  
     tetroxide, 239.  
     valence of, 241.
- Nitrosyl chloride, 256.
- Nitroxy chloride, 257.
- Nomenclature, 101.  
     of acids, 102.  
     of bases, 103.  
     of salts, 104.
- Orpiment, 280.
- Oxygen, 68.  
     family, 126.  
     molecule of, 86.  
     tests for, 72.
- Oxidation, 258, 272.
- Oxides, 215, 347.
- Oxide, arsenious, 273.  
     formula of, 275.  
     properties of, 276.  
     arsenic, 278.
- Oxidizing agents, 249, 255, 258, 286, 289.
- Ortho, 265.
- Ozone, 87.  
     molecule, 89.
- Phenomena, 11.  
     physical and chemical, 13.
- Phosphorite, 266.
- Phosphorus, 146.  
     and electrotyping, 152.  
     and the halogens, 158.  
     molecule of, 156.  
     pentoxide, 261.  
     trioxide, 260.  
     vapor density of, 150.  
     varieties of, 149.  
     valence of, 270.
- Potassium, 96.  
     hydroxide, 96.
- Prussic acid, 317.
- Reaction, classification of, 106.  
     endothermic, 127.  
     exothermic, 127.
- Realgar, 280.
- Reducing agents, 255, 261, 269.
- Reduction, 258, 272.
- Sal ammoniacum, 141.
- Salts, acid, 217.  
     naming of, 104.
- Sand, 330.
- Science, 9.
- Selenium, 123.  
     molecule of, 125.  
     oxides, 232.
- Silicates, 333.
- Silicon, 192.  
     chloride, 197.  
     and carbon, 198.  
     dioxide, 330.  
     and halogens, 197.  
     forms of, 193.
- Sodium, 91.  
     and hydrogen, 93.  
     hydroxide, 94.
- Solution, 78.
- Sulphur, 111.  
     allotropism of, 121.  
     dioxide, 205.  
         bleaching of, 208.  
         formula of, 209.  
         reactions of, 211.

- Sulphur, dioxide, tests for, 210.  
and halogens, 122.  
oxides and water, 213.  
tests for, 115.  
trioxide, 211.  
    formula of, 213.  
    valence of, 213.  
    varieties of, 114  
Symbols, 20, 67.  
Synthesis, 52.
- Tellurium, 125.  
oxides, 232.  
Theory, 60.
- Valence, 202, 351.
- Valence, and heat, 243.  
    positive and negative, 271.  
    variability of, 216.
- Ventilation, 303.
- Volume, unit of, 90, 106.
- Water, 74.  
    formula of, 85.  
    drinking, 79.  
    composition of, 80.  
    gas, 310.  
    purification of, 80.  
    as a solvent, 76.
- Waters, natural, 79.  
    "hard," 303.
- Wood, decay of, 320.

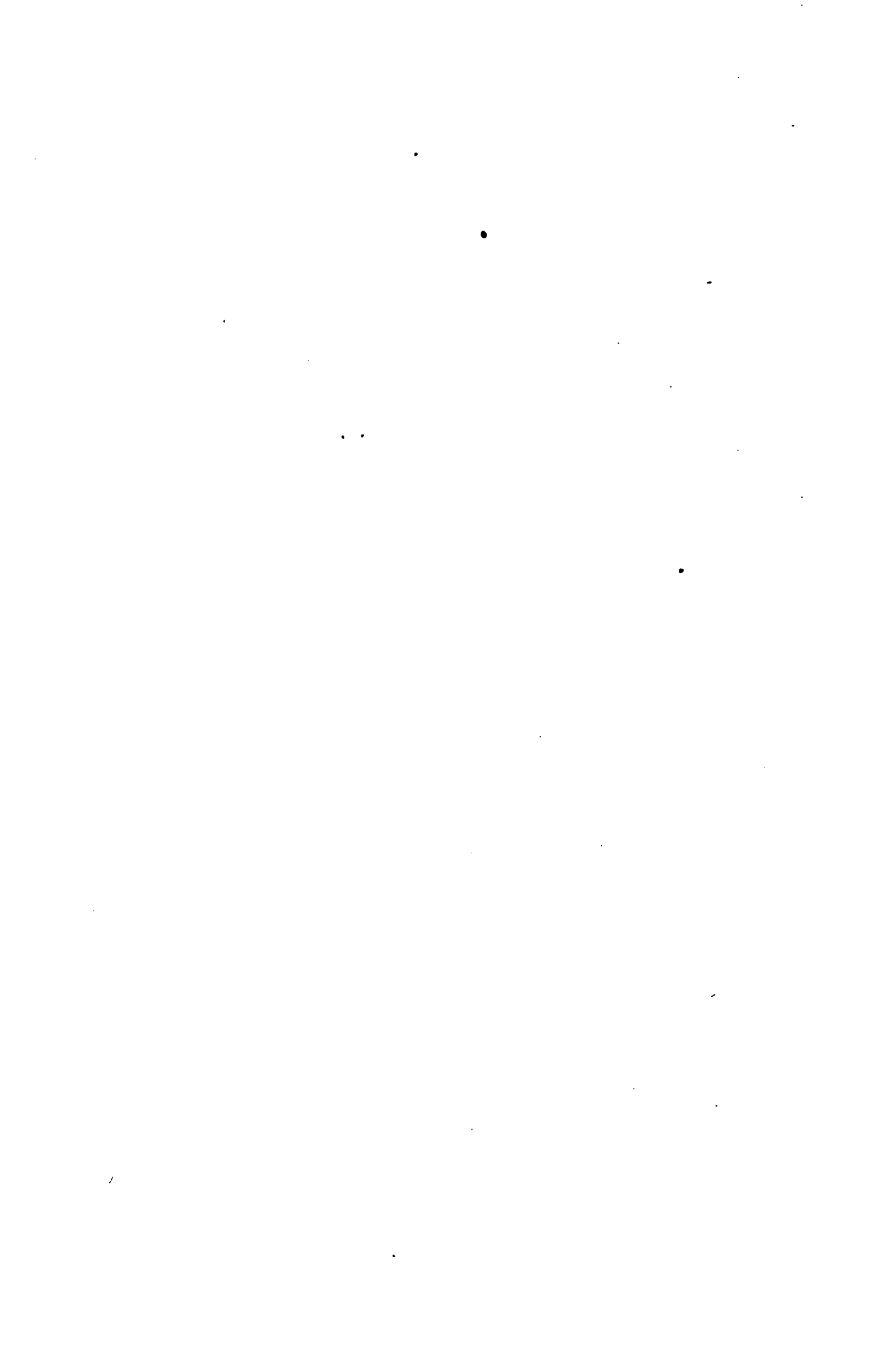












This book should be returned to the Library on or before the last date stamped below.

A fine of five cents a day is incurred by retaining it beyond the specified time.

Please return promptly.

